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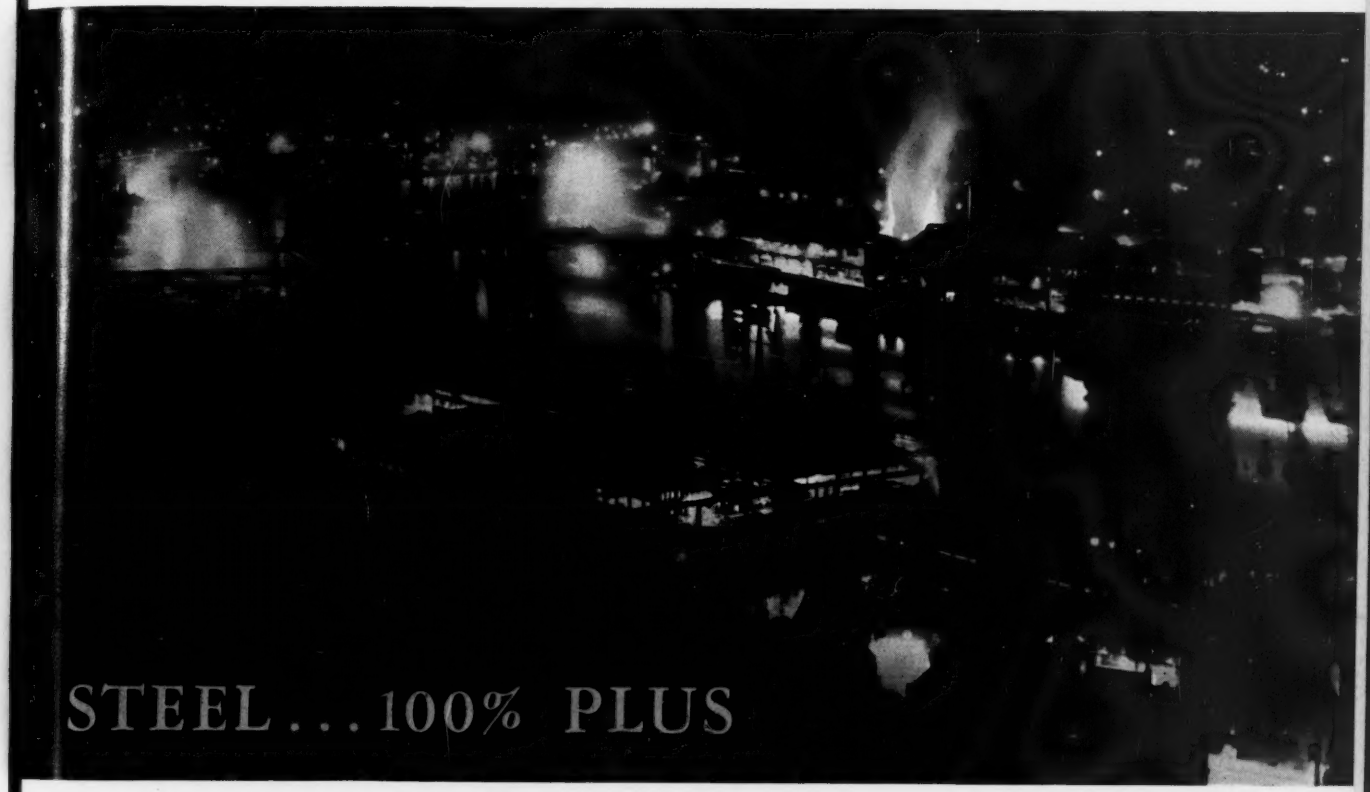
1942

CHEMICAL EDUCATION



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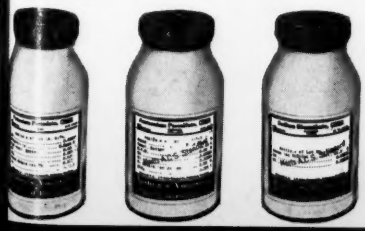

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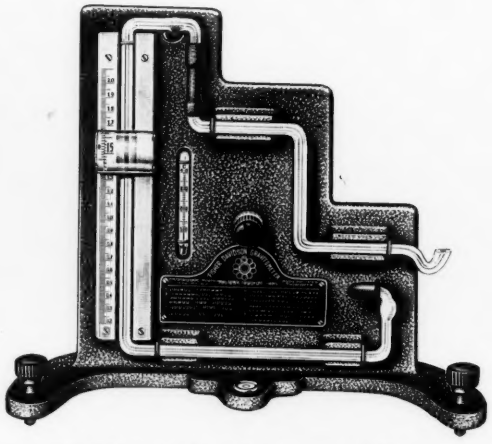

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Manuscript for publication should be directed to the editor. Prospective authors are urged to avoid diffuse writing and to observe the forms outlined in our Notice to Authors of Papers as it appears on page XIV of the January, 1942, issue.
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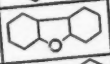
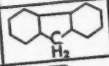
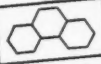
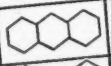
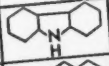
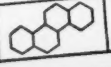
Diphenylene Oxide		95%	81°C.	286°C.	Insoluble	Soluble Hot	Soluble Hot
Fluorene		90%	109°C.	295°C.	Insoluble	Soluble	Soluble
Phenanthrene		90%	102°C.	337°C.	Insoluble	Soluble Hot	Soluble Hot
Anthracene		98%	213°C.	341°C.	Insoluble	Soluble Hot	Soluble Hot
Carbazole		97%	243°C.	353°C.	Insoluble	Soluble Hot	Soluble Hot
Chrysene		—	245°C.	440°C.	Insoluble	Insoluble	Soluble Hot

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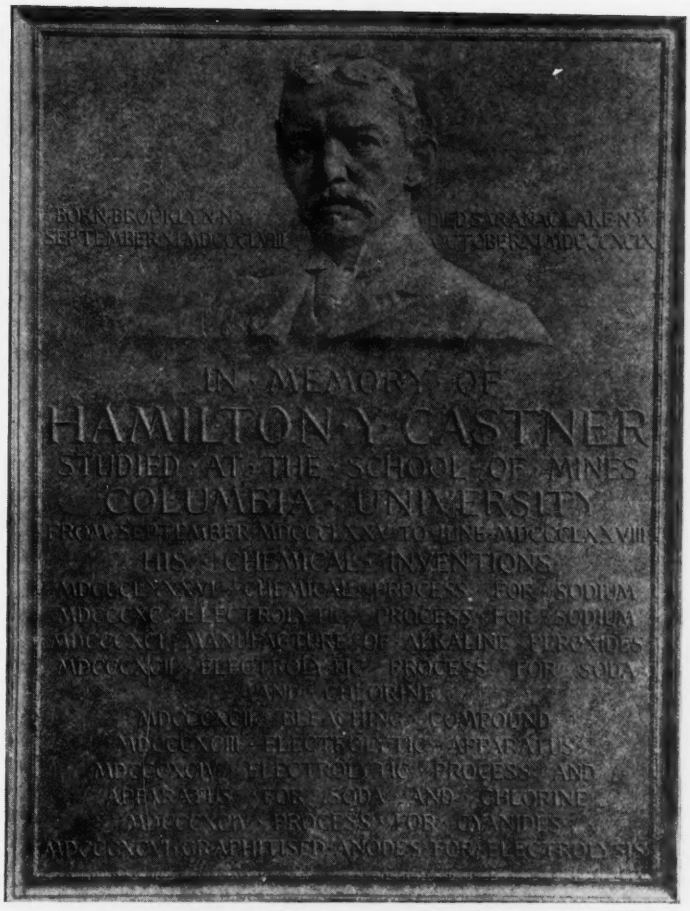

From School of Mines Quarterly, Columbia University, XXV (1904)

Hamilton Young Castner
(1858–99)

Bronze Tablet in Havemeyer Hall, Columbia University

(For further information about Hamilton Young Castner, see page 353.)

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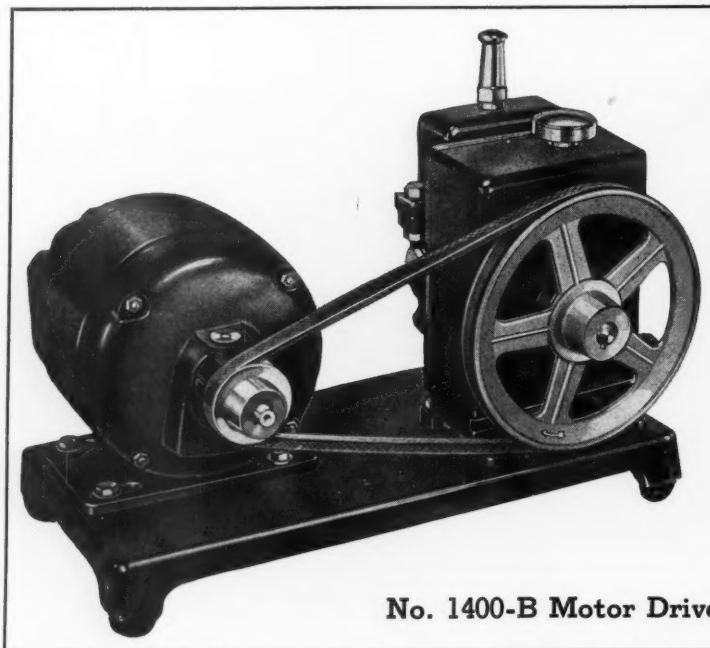

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Editor's Outlook

SO MUCH has been said lately about this being "a physicist's war" that we are in danger of losing sight of the fact that the chemist is still going to be a pretty handy person to have around. We have no desire to belittle the efforts of our brother-in-arms, the physicist, and grant him his position of superior importance—for the moment, at least—in the armed forces. We recently called attention to the serious shortage of teachers of physics and the difficulties involved in the remedy of this situation. We are glad to note the efforts that are being made this summer, through courses given in the ESMDT program, to further the training and experience of prospective physics teachers.

But to return to the chemist. Many people—and some of them, unfortunately, in positions of high authority—have been unimpressed by the available supply-and-demand figures for chemists, feeling that they have not been sufficiently definite and explicit. Anything that can be added to the argument, to show the definite demand of industry for trained chemists, is important right now. Some studies and announcements made by the U. S. Bureau of Labor Statistics are worth reviewing. It has been pointed out that predictions made by the Bureau have been uniformly more accurate than those of practically all other agencies.

An effort was made to survey the employed personnel of industry throughout the country, especially to determine the proportion of college-trained employees in certain categories: engineering, accounting, management, "science." Scientists included chemists, physicists, mathematicians, physicians, and dentists. It was found that 2.4 per cent of all employees were college-trained, and of this group 15 per cent (or three-fourths of the "scientists") were chemists.

Dean A. M. Greene, of Princeton University, made a rather more detailed survey, with the cooperation of the Bureau of Labor Statistics. His figures covered almost a million employees and showed the percentages of college-trained "scientists" in various industries as follows:

	Per cent		Per cent
Machine industry	0.2	Textiles	0.1
Non-ferrous metals	0.7	Food	0.7
Iron and steel	0.8	Chemical and petroleum	2.5
Stone, clay and glass	0.7	Public utilities	0.1
Paper and products	1.5	Miscellaneous	1.2

Accepting the result of the study previously cited, that three-fourths of industrially employed "scientists" are chemists, one can calculate for himself the proportions in the various industries.

On the basis of estimates of industrial expansion during 1942, and the number of new employees that this will necessitate, Dean Greene reported recently to the Society for Engineering Education that 80,000 new engineers would be wanted this year. He also estimated 15,000 as the needed number of "scientists" and if three-fourths of these are to be chemists it poses us the problem of finding 12,000 chemists in short order. According to best estimates, about 8000 were just graduated from institutions accredited by the A.C.S.

But the Bureau of Labor Statistics gives us no respite, and tells us that the numbers employed in war industries will *double* by the end of 1943 to the astounding total of some 20 million. While it is not safe simply to multiply the preceding estimates by two, since there will be a certain amount of transfer of personnel from other industries, still it is perfectly evident that 1943 will see a greater demand for trained technicians than 1942.

OCCUPATIONAL Bulletin No. 10, recently issued by the national office of Selective Service, is by far the strongest representation which headquarters has yet made to local selective service boards relative to the urgent and critical need of scientific and specialized personnel in industry. It has been reproduced in full and ably commented on in the July 10 issue of *Chemical and Engineering News*, which should be seen by all students and teachers of chemistry. There is nothing new in the suggestion that chemists engaged in necessary work in critical industries, as well as students well along in their training for such work, should be considered for occupational deferment. It is the greater strength, and apparent urgency, of this last directive that is encouraging. And, for the first time, the value of graduate training is mentioned. Graduate students of chemistry, if they are "assistants" with teaching responsibilities, are marked as special candidates for deferment. The necessity of *training* chemists is particularly emphasized.

As Dean Whitmore says in his letter, which we are reproducing in this number (page 395), this should make clear to every student of chemistry where his duty lies: to stay out of the reserve and prepare himself for industry. But we anticipate that in far too many cases the lure of a uniform and commission, and the call to more violent and spectacular action will prove irresistible. In default of any organization or method, as yet, to give glamour or adequate recognition to the civilian service of production, *we* must persuade our students that the national interest is best served by their staying on the job. We will meet plenty of competition; it will be difficult, but necessary.

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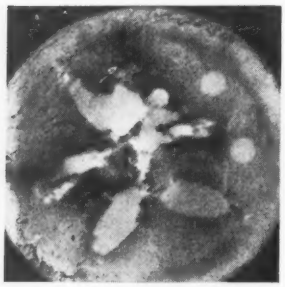
What's Been Going On

Metals Give Up Secrets

THE PHOTOGRAPHIC action of radiations from radioactive phosphorus recently was used by Dr. William E. Shoupp, Westinghouse research physicist, to determine the distribution of this element in steel. He found that phosphorus, an embrittling agent, concentrates inside minute air pockets or blowholes in steel. The same method can be used to show distribution of sulfur, manganese, silicon, and any other constituents of steel that can be made radioactive. A complete analysis in this way conceivably will lead to improved methods of making steel and all kinds of alloys.



Radioactive phosphorus leaves its tracks in a disc of steel. Light areas represent concentrations of phosphorus. The picture was made by clamping the disc to a sheet of film and storing it for several hours in an ordinary tin can.

Courtesy of "Research Progress"

Using radioactive silver and gold, William A. Johnson made other experiments in the Westinghouse laboratories to find out how one metal diffuses into another to form an alloy. Explanations of how an alloy can be stronger than any of its constituents are based merely on theoretical evidence. Johnson seeks a practical understanding of the way in which the atoms of one metal line up with those of another metal to form a homogeneous combination.

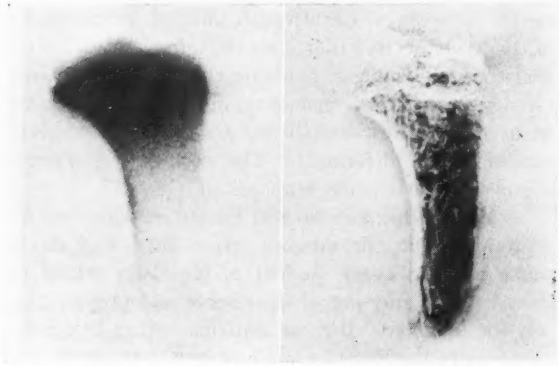
Distribution and relative concentration of various elements in ores has been revealed by making these elements radioactive. Because of their economic and strategic importance, native manganese, arsenic, copper, tungsten and gold ores have been analyzed in this way by Clark Goodman and George Thompson at Massachusetts Institute of Technology. It is likely that an extension of their experiments will help to unravel some of the deep mysteries of the geologic formation of minerals.

—RESEARCH PROGRESS

Courtesy of "Research Progress"

DISTRIBUTION OF METALS

Distribution of tungsten in wolframite ore is shown by the radioautograph at the right. Such pictures divulge information helpful in refining such ores and may tell tales of the geologic formation of minerals.

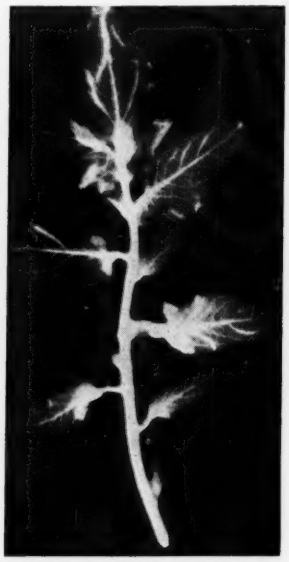


Courtesy of "Research Progress"

SECTIONS OF RAT BONE

Bones are made of materials that must be renewed continuously, finds Professor David M. Greenberg, of the University of California. He has found that vitamin D acts partly by favoring absorption of calcium from digestive tracts, and partly by a direct effect on mineralization of bone. Comparison of a radioautograph (left) with a normal section of a rat bone shows that the most active part of the tissue biologically is most active in retention of the radioactive bone replacement materials.

In research on stable, non-radioactive isotopes the measurement of isotope ratios is always important and often difficult. With deuterium, this can be done by measuring the density of the "heavy water" formed on combustion, but with other elements, such as C^{13} or N^{15}, the mass spectrometer is virtually the only means of making a determination. Until recently there have been no suitable mass spectrometers on the market, for routine use. They are now available, however, and work in this field has been greatly stimulated. But in addition to its use in tracer studies the mass spectrometer is finding applications in other fields as well. It is particularly valuable as a sensitive instrument for gas analysis. Furnace atmospheres and various reaction mixtures have been studied by means of this instrument, which can show the presence of a gaseous constituent in extremely low concentration by the formation and detection of ions of characteristic mass. Considerable research is also being carried on in the study of hydrocarbon mixtures with the mass spectrometer.



A tomato plant grown in a solution of radioactive sodium phosphate by Dr. Perry Stout at the University of California. Light areas are accumulations of radiophosphorus. The leaves were removed from the plant 36 hours after the radioactive material was added to the nutrient solution.

Courtesy of "Research Progress"

Hamilton Young Castner (1858–99)

A Forgotten Pioneer of the Aluminum Industry

VIRGINIA HALTON LORD[1]

Massachusetts Institute of Technology, Cambridge, Massachusetts

IN WARTIME, aluminum can no longer be taken for granted. As almost overnight it drops its character of a familiar, everyday article and resumes its former role of a rare and precious metal, it might be interesting and timely to glance briefly at its history; to recall the days when another generation did without aluminum, not for reasons of defense, but because its cost was prohibitive; to honor again the man who was first able to reduce its cost substantially enough to give industry and mankind one of the most useful metals.

Although the process which enabled Hamilton Young Castner to capture the aluminum market for two years is still listed under his name in the standard dictionaries, little readily available information can be found about the man himself. Reference books seem to indicate that if he is not unknown, at least he is forgotten. True, there is a bronze tablet to his memory in Havemeyer Hall at Columbia University, where, at the unveiling, Castner's contemporaries extolled him and his achievements with marked sincerity and enthusiasm. Several of his basic processes in daily use throughout the world still testify to his inventive genius, but the bare facts of his life, of his work, of his character, and personality have yet to be recorded in one place and made easily accessible. This apparent neglect of Castner by posterity may be traced partly to the fact that our country is still young, and in its brief life the accomplishments of its people are many—particularly in the fields of science and technology. There simply has not been time for the tales of all our pioneers, heroes, and innumerable benefactors of mankind to be told. Another reason for Castner's obscurity—and this is doubtless the chief reason—is that his achievements were wiped out with startling suddenness by an entirely new and radically different process that reduced the cost of aluminum below that which his had made possible. In a short-range view of the history of aluminum, Castner and his work might be overshadowed. But in a long-range view, he finds his rightful place in the difficult struggle of over half a century to bring to the masses a new and highly promising metal; his insight, his skill, his patient and conscientious pioneering, his ultimate success—brief as it was—where so many had failed, his later triumphs, all are seen in their proper perspective and given the importance that is clearly due them.

[1] Present address: Supplementary Research Center, Director of Weather, Headquarters Army Air Forces.

Hamilton Young Castner, the second son of Samuel and Julia A. Castner, was born in Brooklyn, New York, on September 11, 1858. He prepared at the Brooklyn Polytechnic Institute for admission to the School of Mines, Columbia University. He entered the School of Mines in September, 1875, as a regular student in the course of analytical and applied chemistry, but he never took his degree. During his second year, he became impatient of the varied work required for the baccalaureate and began to devote his entire energy and attention to the study of chemistry under the distinguished dean of the school, Dr. Charles F. Chandler. Chandler's several addresses in honor of Castner in later years fully attest the teacher's personal and professional admiration for his former student.

As an undergraduate, Castner displayed an "earnest devotion to work" and a conscientious effort to succeed; "his perseverance in face of difficulties and...determination to accomplish the desired results"[2] were outstanding traits of his character. He was never concerned with the easiest way; he wanted only the best way and was tireless in his attempts to find it. Dr. Marcus Benjamin, a classmate of Castner's, told the story of finding Castner one day outside the Dean's office with a wagon and a load of bottles. When he sought an explanation, he was told that the bottles were to be used to collect samples of water from all the wells then in existence in the city of New York. He argued that since Castner was not an applicant for a degree, such work was an absolute waste of time, but Castner persisted with his plan, and as a result the Board of Health, of which Dr. Chandler was then President, soon ordered closed all wells used as a source of drinking water. The fact that the health of the municipality improved can doubtless in large part be traced directly to this instance of Castner's devotion to duty.

A somewhat unexpected side to Castner's nature is the interest he manifested in boating. During his first year at Columbia, he "pulled bow on the first freshman crew that Columbia ever sent to an intercollegiate regatta."[3] He also served as "coxswaine to the four-oared crew that won in the Harlem regatta in June, 1877, and...acted in a similar capacity to the

[2] BENJAMIN, *Columbia School of Mines Quarterly*, **XXV**, 215 (1904).

[3] *Ibid.*, p. 215.

eight that yielded to Harvard at Springfield a few days later."[4]

At the end of three years, Castner left Columbia to begin work as an analytical and consulting chemist in his own laboratory in Pine Street, where he rapidly secured recognition and standing. His initial work was chiefly routine analysis of fertilizers. An incident which reveals the character and ability of the young man is told in connection with the first analysis which he made in his laboratory. He had completed his work and checked his results, but still fearful of error, he sent a sample of the material to a neighboring chemist of considerable reputation. The report which came back was at variance with the data he had obtained. The young chemist began to experience grave doubts of his own ability. After consulting with his close friend, Dr. Benjamin, he finally decided that his original findings must stand. He felt that if he were incompetent, the sooner the fact was proved, the better. But, as Dr. Benjamin relates, Castner was not incompetent, and the results of his analysis brought him his first commercial success and a customer who henceforth had the utmost confidence in him.

When Castner was not occupied with the rapidly increasing analytical work, he devoted himself to experimenting in an effort to improve certain chemical manufacturing processes. The first of such experiments which revealed the peculiar bent of his genius was an electrical process for manufacturing animal charcoal. He was unable to market the process, promising as it seemed, chiefly because of the "depressed financial condition of the country" at the time and because the "larger firms engaged in that business consolidated and reduced the price below that on which his calculations were based."[5] He obtained notable success, however, when he began to devise new and improved methods for preparing alkaline products and to discover new uses for them. In 1886 he invented his process for manufacturing sodium, which was first announced in the New York *World*, May 16, 1886. The newspaper article mentions Castner as being well known in New York as a "chemist of high standing" with a laboratory at 218 West 20th Street, and as having associated with him Mr. J. H. Booth and Mr. Henry Booth, both well known "as gentlemen of means and integrity."[6] The process was soon to receive commendation from the leading chemists in the world. The patent for it was taken out in the United States in June, 1886, and in addition to being the first one granted in this particular field in this country, was probably also the only one taken out in the world since 1808. Castner delivered a lecture on his process at the Franklin Institute on October 12 of the year of his invention, and later the Institute bestowed on him a gold medal in recognition of the benefit to science accruing from his work.

Sir Humphrey Davy had discovered sodium in 1807, but until Castner devised his chemical process for producing it, all methods of making it had been almost prohibitive in cost. Sainte-Claire Deville had discovered that a practical way to make aluminum was by reducing aluminum chloride with metallic sodium. He had been unable to perfect a method for producing sodium inexpensively, however, even with several million francs from the treasury of France and the support of Louis Napoleon.

It took three pounds of sodium to make one pound of aluminum. Consequently the extent of the production and use of aluminum necessarily paralleled that of sodium. Since its discovery in 1827 by Wöhler, outstanding chemists of the world had been trying to invent a process for producing aluminum cheaply. Figures representing the degree of their success are interesting. In 1856, aluminum cost $180 a kilogram, in 1857, $60, and by 1883 the price had fallen to $18.[7] It was Hamilton Young Castner, of New York, who finally obtained truly gratifying results, who was able to produce sodium for about twenty-five cents a pound, and, by employing this cheap sodium in a process similar to Deville's, to put aluminum on the market for about a dollar a pound.

Because the charcoal which was used in earlier experiments for making sodium was lighter than the soda used, it floated on the surface and failed to effect the reduction of the soda. Castner discovered that carbide of iron had about the same specific gravity as caustic soda. By substituting, then, caustic soda and carbide of iron for carbonate of soda and charcoal, he developed a process at once simple and effective that could be worked at a very moderate temperature in steel crucibles which could be used more than a hundred times.

Castner's outstanding success in making large-scale production of aluminum possible cannot be attributed to accident or chance. His process was the result not only of insight and inventiveness, but of the courage and pertinacity needed to carry out long, careful, and thorough investigation in a field which already seemed fairly well covered. Again it is Dr. Benjamin who provides detailed information. He mentions how the files of Wagner's *Jahresberichte* and the proceedings of the London, Paris, and Berlin chemical societies were painstakingly examined for every reference to the matter of Castner's invention and how they were "carefully considered and discussed from every point of view for the purpose of gaining some information that would improve his process."[8]

Unable to obtain capital for erecting a plant in this country, Castner went to England during the winter of 1886–87, and there he built and worked a sodium furnace in a small experimental works near Waterloo

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[4] BENJAMIN, *op. cit.*, p. 215.
[5] *Ibid.*, p. 217.
[6] As quoted in RICHARDS, *"Aluminum, its history, occurrence, properties, metallurgy, and applications, including its alloys,"* 2nd ed., Henry Carey Baird and Company, Philadelphia, **1890**, p. 168.
[7] FLEURY, "The past and the future of aluminum," *Popular Science Monthly*, **44**, 400 (1893).
[8] BENJAMIN, *op. cit.*, p. 217.

Bridge. The inventor was assisted in this undertaking by Mr. J. MacTear, F.C.S., who, in March, 1887, read before the Society of Chemical Industry a description of the furnace and the results obtained with it. Almost immediately upon demonstration of Castner's process, the Aluminum Company, Ltd., of Oldbury, near Birmingham, was formed, with Castner as managing director.[9] Castner then captured the market for aluminum, and for two years had the monopoly of its manufacture. He finally reduced the cost of the metal to about eighty-five cents a pound.[10] His process suddenly became useless, however, and his manufacture was forced to an abrupt end when Charles M. Hall, of Oberlin, Ohio, proved he could produce aluminum without the aid of sodium at a much lower figure. Hall's new process was one involving electrolysis.

The integrity of Castner's character, his resourcefulness, and courage are revealed in the way in which he met this telling blow of misfortune. "There had been created a company with a large amount of capital, and the stock had been widely distributed, a great deal of which, as is usual in such cases, was held by 'widows and orphans.' "[11] Castner felt his moral responsibility very keenly and immediately began to devote his energies to saving the company and to placing it on a safe financial footing by improving methods of producing sodium and by finding new uses for it. Very soon he found that sodium was valuable in medicinal preparations made from coal tar and in certain other drugs. Then he invented a process for converting sodium into peroxide for bleaching purposes. He began to apply his cheap sodium in the preparation of pure cyanides. The commercial cyanides at that time contained only 50, 60, or 70 per cent pure cyanide. Castner discovered that he could put on the market pure cyanide at a price no greater than the impure had formerly cost. The pure cyanides were employed in electroplating and gilding, and in the electrodepositing of metals, but found even wider application in the extraction of low-grade ores.

In 1891, Castner invented a new process for the manufacture of sodium and potassium by the electrolysis of caustic soda and caustic potash. According to Dr. Chandler, Castner's process was based on Sir Humphrey Davy's.[12] Davy had never been able to produce sodium in any quantity, and the difficulties of his method were so great that it had been entirely abandoned in favor of chemical methods until Castner studied it and with his usual skill overcame the obstacles to its success.

[9] A full description of the plant was given in an address delivered before the Society of Arts, March 13, 1889, by William Anderson and in a discourse at the Royal Institution, May 3, 1889, by Sir Henry Roscoe, President of the Company. Excerpts from these addresses may be found in RICHARDS, *"Aluminum, its history, occurrence, properties, metallurgy, and applications, including its alloys,"* 2nd ed., Henry Carey Baird and Company, Philadelphia, **1890,** p. 174 f.

[10] RICHARDS, *Columbia School of Mines Quarterly,* **XXV,** 219 (1904).

[11] CHANDLER, *J. Ind. Eng. Chem.,* **3,** 145 (1911).

[12] CHANDLER, *Columbia School of Mines Quarterly,* **XXV,** 209 (1904).

Castner, indefatigable, and with his expected ingenuity, next turned his attention to the preparation of caustic soda and chlorine by electrolysis of a solution of common salt. Perhaps a hundred or more different plans had been suggested and as many forms of apparatus devised for making caustic soda before he developed the following simple process: Through the use of mercury at the cathode, the metallic sodium from the electrolyzed sodium chloride is carried away in an amalgam and subsequently, in a series of cleverly designed cells, is converted into very pure caustic soda.

Castner's process was the first to be completely successful, and once again he had solved a problem which had baffled French, German, English, and American chemists for as many as forty years. The American patent for the apparatus was granted in April, 1894, and the patent for the process in October of the same year. As a direct result of this invention our country was able to manufacture bleaching powder for the first time in its history. Previously it could not be produced at a price low enough to compete with that of the same product made in England and on the Continent. Another improvement resulting at this time from Castner's inventive genius was the use of graphitized anodes in electrolysis. The disintegration of ordinary carbon anodes had been a serious problem with chemists. Castner found it a relatively easy procedure to convert the carbon into graphite, which could resist the action of solutions.

At Columbia in 1902 on the occasion of the unveiling of the tablet to the memory of Castner, Dr. Benjamin said:

> "The splendid success of his genius found its culmination in the extensive plant that bears his name at Niagara, and it was a glad moment when my colleagues on the Jury of Chemical Products at the Pan American Exposition in 1901 unanimously agreed with me in conferring the highest award possible on the Castner Company."[13]

In that year nearly one-sixth of all the power generated at Niagara Falls was utilized by the two industries founded by Castner. Three and a half dollars' worth of common salt, through his process, could be converted into about forty dollars' worth of caustic soda and about fifty dollars' worth of bleaching powder. The forty dollars' worth of caustic soda could furnish, through his inventions, nearly one thousand dollars' worth of metallic sodium. This, then, is the mere monetary measure of Castner's benefits to mankind, but through the monetary measure are immediately suggested the many ramifications of such progress.

When Castner's health began to fail in 1898, he went to Florida for the winter, and later to Saranac Lake in the Adirondack Mountains, where a month after his fortieth birthday on October 11, 1899, he died of tuberculosis, the disease that had previously brought death to his father and two brothers. He had no children, but was survived by his wife.

[13] BENJAMIN, *op. cit.,* p. 218.

The obituary which appeared in the *Journal of the Society of Chemical Industry*, concludes that he

"was one who has left the impress of his knowledge and ability on the chemical manufacturing industries, not only of this country, but also on those of the Continent and of America . . . a friend of many, keen of wit, generous almost to a fault, a man whose word was beyond question."[14]

[14] *J. Soc. Chem. Ind.*, **18**, 901 (1899).

Dr. Joseph W. Richards, Professor of Metallurgy at Lehigh University, said that Castner possessed

"not only the insight, the pertinacity, the courage, the mind of a great inventor, but also what very few inventors do possess—the industrial spirit; the power not only to devise but to build; the power not only to invent, but to manage and erect. He was a leader of the industrial world as well as a leader in the inventive world—a combination so rare that but few of our great Americans possess it."[15]

[15] RICHARDS, *op. cit.*, p. 220.

A SIMPLIFIED PREPARATION OF SCHWEITZER'S REAGENT

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THE wide use of the artificial fiber in industry has made the study of this product a "must" even in elementary courses of chemistry or general science. Schools which demonstrate the production of artificial fibers usually use cellulose regenerated from Schweitzer's reagent as the simplest means of showing this phenomenon. The demonstrator merely squirts some of the prepared solution into a dilute solution of sulfuric acid to produce crude cords of cellulose. It is even possible to dissolve the cotton in the solution in front of the class and complete the process within ten minutes. The crude, thick threads thus formed have the advantage of being visible across the room.

Unfortunately, Schweitzer's reagent is difficult to prepare and keep, and involves the discomfort of working over concentrated ammonia. Many of the discomforts of the common process may be avoided by using a simple apparatus based upon the work of Sakostchikoff,[2] who used a weak Schweitzer's reagent to swell fibers as an aid in their analysis. Sakostchikoff contributed, among other interesting points, the fact that the dissolving power of the reagent is a function of the Cu ion concentration, and that the ammonia concentration is not important, providing it is above 6 per cent. This is contrary to the common belief that the ammonia concentration must be very high, as much as 28 per cent.

The operation of the apparatus is simple. Air is bubbled through two bottles of limewater to remove carbon dioxide. It is then bubbled through a tower containing copper metal in 28 per cent ammonia. Schweitzer's reagent, strong enough to be used for the demonstration, is formed in about two hours. To remove fumes, the air train may then be run into a weak sulfuric acid solution with a capacity of 500 cc. Ample material for the several demonstrations is provided.

The tower is made of very large glass tubing, such as a broken one-liter graduated cylinder. A three-holed stopper in the top carries a long inlet tube reaching to the bottom of the tower, a short outlet tube, and a dropping funnel for filling and washing the tower. A one-holed stopper in the bottom is provided with a glass stopcock for draining. The tower is then filled with copper turnings, gauze, or wire. It is cleaned by rinsing with dilute nitric acid and water without removing the copper, and is put away complete until the next term when it is similarly cleaned and is ready for use.

This method of producing Schweitzer's reagent involves only three short steps, compared with seven lengthy operations for the older process. The resulting reagent has an ammonia concentration of about 15 per cent, which is not irritating to the eyes, yet quite as strong as 28 per cent ammonia in dissolving power. The solution can be run into an Erlenmeyer flask in the classroom without causing trouble.

In actual practice at our school, cotton is dissolved in the solution until the solution is saturated but not too viscous. It is then squirted out of a small wash bottle with a pressure bulb. The receiving solution is a 1:10 solution of sulfuric acid in a flat tray. Cords of cellulose, one-eighth inch thick and from four to twelve inches long, are formed, which decolorize in five minutes.

The process is simple to operate, uses a minimum of materials, involves less time and care, gives a less irritating solution, and leaves a cleaner laboratory than the older method of preparing this solution for classroom demonstration.

[1] Present address: Corporal A. Breslau, Balloon Barrage School Detachment, Camp Tyson, Tennessee.

[2] SAKOSTCHIKOFF, *Milliard Magazine*, **I**, 882 (1929).

The History of Chemistry in Arkansas[1]

HARRISON HALE *University of Arkansas, Fayetteville, Arkansas*

P. G. HORTON *Henderson State Teachers College, Arkadelphia, Arkansas*

THE history of chemistry in Arkansas as practiced by the white man may very well begin with the manufacture of salt by De Soto and his followers in the summer of 1541. This is described by the "Gentleman of Elvas" who was a member of De Soto's band who records in his diary (*1*) that the party visited Hot Springs and "the horses drank of a lake of hot water and somewhat brackish." He further described the process by which the Indians of that region, which is now Arkansas, obtained salt

> ". . . until that time the Christians wanted salt, and there they made great store, which they carried along with them. The Indians do carry it to other places to exchange for skins and mantles. They make it along the river, which, when it ebbeth, leaveth it upon the upper part of the sand. And because they can not take it without much sand mingled with it, they throw it into certain baskets which they have for the purpose, broad at the mouth and narrow at the bottom, and set it into the air upon the bar, and throw water into it, wherein it falleth. Being strained and set to boil upon the fire, when the water is sodden away, the salt remaineth in the bottom of the pan."

This record has been carefully checked and undoubtedly the location of the salt deposit is near Arkadelphia and not very far from the present site of Hot Springs. When it is recalled that this was in the sixteenth century, it is not at all impossible that this may have been the first preparation of salt by white men in the New World.

Hot Springs today is visited by thousands each year, many of whom find renewed health by the use of its waters. The approximate chemical composition of the hot water used from the 47 springs, similar in analysis, is given in the "Circular of Information" issued by the Department of Interior (*2*):

APPROXIMATE CHEMICAL COMPOSITION OF THE HOT SPRING WATERS AT HOT SPRINGS, ARKANSAS

Constituents	*Parts per Million*	*Constituents*	*Parts per Million*
Silica (SiO_2)	46	Sulfate radical (SO_3)	7.8
Iron and aluminum (Fe + Al)	0.2	Nitrate radical (NO_3)	0.4
Manganese (Mn)	0.3	Nitrite radical (NO_2)	0.002
Calcium (Ca)	47	Phosphate radical (PO_4)	0.05
Magnesium (Mg)	5.1	Borate radical (BO_2)	1.3
Barium (Ba)	Trace	Arsenate radical (AsO_4)	None
Strontium (Sr)	Trace	Chlorine (Cl)	2.5
Sodium (Na)	4.8	Bromine (Br)	Trace
Potassium (K)	1.6	Iodine (I)	Trace
Lithium (Li)	Trace	Fluorine (F)	None
Ammonium (NH_4)	0.04		285
Bicarbonate radical (HCO_3)	168		

[1] Presented before the Division of the History of Chemistry at the 103rd meeting of the A. C. S., Memphis, Tennessee, April 21, 1942.

On November 12, 1941, only seven months ago, there died in Murfreesboro John Huddleston, the man who owned the field where the diamonds of Arkansas have been produced. He discovered the first diamond on August 8, 1906, which proved to be a steel-blue gem weighing $1\frac{3}{8}$ carats. Refusing to sell this stone, when first discovered, for fifty cents to a business man in the nearby town, Huddleston later sold the entire property for an amount that made it possible for him to spend the remainder of his days in comfort (*3*).

Not far from these localities southwest of Little Rock there occurs a region of unusual geological interest that is called Magnet Cove. This has been frequently studied by geologists and numerous articles have been written describing the wide variety of minerals and the unusual geological formations occurring in an area of about five square miles (*4*).

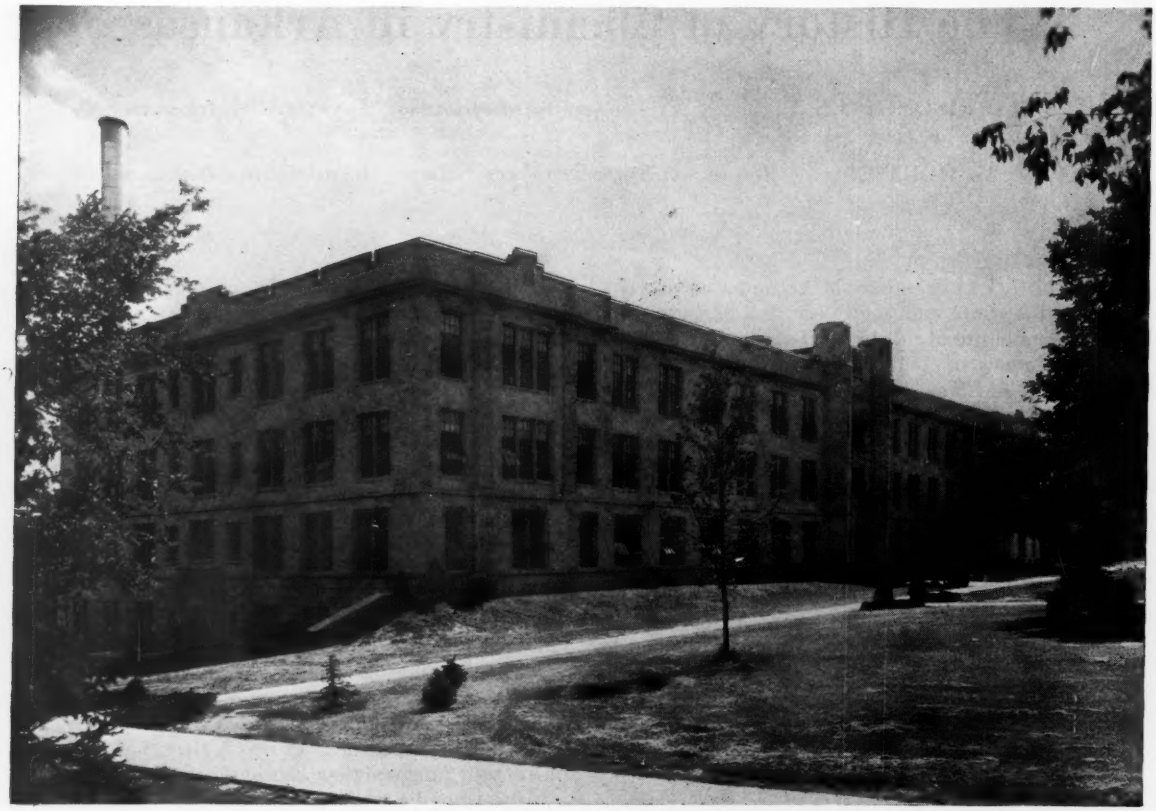
Also close by is the bauxite area of Arkansas in Saline and Pulaski counties from which there has come year after year for some time almost all of the bauxite mined in the United States. The production in 1941 apparently was more than 90 per cent of the American total of a record high—an estimated 900,000 tons (*5*).

In 1886 in Ohio, Charles Martin Hall first obtained metallic aluminum by the electrolysis of aluminum oxide in fused cryolite. The next year important deposits of bauxite in Pulaski County, Arkansas, were identified by John C. Branner, State Geologist. Announcement was not made, however, till 1891 and production of Arkansas bauxite did not begin till 1899 (*6*). In the early days no rotary kilns were available and so before shipment the ore was dried by building log fires on either side of piles of ore and keeping them burning constantly for 72 hours.[2]

The discovery of manganese in another section of the state, in Independence County near Batesville in 1849, is described in an early report of the Arkansas Geological Survey which is a classic (*7*). The first large shipments did not begin till 1881. In 1887 Arkansas ranked third in the United States in manganese output, with continuous production since that time. Zinc, mercury, and other metals, as well as silica of unusual purity are produced in widely scattered sections of the state.

The production of oil from the Busey well near El Dorado in January, 1921, started an industry still very active, giving the state in some years the position of fourth in the country with respect to barrels produced (*8*).

[2] CROSS, personal correspondence.



CHEMISTRY BUILDING, UNIVERSITY OF ARKANSAS

EDUCATIONAL

In 1850 St. John's College was founded in Little Rock under Masonic influence and in 1852, in the northwest section of the state, Cane Hill College was opened at Cane Hill and Arkansas College at Fayetteville. Of course, all of these colleges were suspended during the Civil War. The buildings of Arkansas College were burned and the college ceased to exist. St. John's College was reorganized in 1869 but is not in existence now. Cane Hill College was later reorganized and then transferred to Arkansas Cumberland College now located at Clarksville as the College of the Ozarks.

Probably college chemistry was first taught in the state at Cane Hill. This is based upon a statement in the catalog of the College for 1858–59 which gives the text as that of Silliman.[3] When the University of Arkansas was established the chief contestants for the location were Fayetteville and Batesville. After Fayetteville had been chosen a college was established at Batesville under the general direction of the Southern Presbyterian Church and is still giving active service under the name of Arkansas College. In its oldest available catalog, that of 1875, chemistry is listed as one of the subjects taught.[4] It is claimed that a coat worn by an early professor there "became so stained and streaked with chemicals that it was looked upon as an infernal machine that might explode at any time!"

For more than a decade no other institution of higher learning now active in the state seems to have been started; following this period a group of institutions, sponsored by the various denominations, came into existence within a few years of each other. Central Collegiate Institute at Conway in its announcement for 1886–87 states that chemistry is required in the junior year for an A.B. degree, that the main experiments are performed before the students and that "we aim at a practical and thorough knowledge of the every day facts of science rather than a smattering of extended theories." Science was one of the six departments in the college and Steele's textbooks were used.[5] Chemistry has been taught continuously since that time and now has an important place in the relatively new Science Building at Hendrix College, the modern name of the old institute. "Ouachita Baptist College, male and female," states in its second annual catalog for the session for 1887–88 that "natural philosophy or physics

[3] HURIE, WILEY LIN, President, College of the Ozarks, personal correspondence (1/23/42).

[4] HALL, MISS JUNE, Registrar, Arkansas College, personal correspondence (1/24/42).

[5] MCHENRY, M. J., personal correspondence (1/30/42).

comes in the fall terms and is a necessary introduction to the study of chemistry . . . . Chemistry is in the spring term."[6]

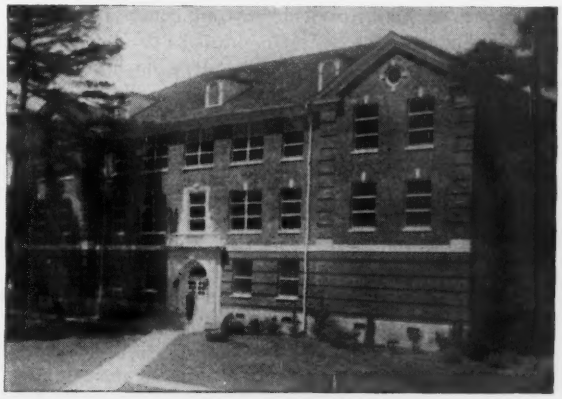
A second Methodist Institution was founded in 1890 at Arkadelphia with a semester of chemistry taught by the President, G. C. Jones, using Youman's text. A picture of the early lecture room gives a good idea of the equipment of 50 years ago. Arkansas Methodist College later became Henderson and then Henderson-Brown College and its site and buildings are now occupied by Henderson State Teachers College, where chemistry is housed in a new and well-equipped Science Hall. In 1891 with a heritage from Cane Hill College, Arkansas Cumberland College, now the College of the Ozarks, was opened in Clarksville. It, too, has a chemistry department in a relatively new Science Building.

The legislature in 1909 authorized the establishment of four state agricultural high schools. These were opened in 1910 at Russellville, Jonesboro, Monticello, and Magnolia. The school at Jonesboro became a Junior College in 1918 and a Senior College in 1925. While chemistry was not taught at first, numerous courses in a well-planned curriculum have now been given for a number of years.[7] The A and M College at Monticello has now become a Senior College but that at Magnolia and the Arkansas Tech at Russellville are still maintained as junior colleges. In each of these institutions chemistry has had, in recent years, a prominent and well-maintained position in a comparatively new and well-equipped laboratory.

The University of Arkansas observed its seventieth anniversary on January 22.

"It owes its origin to a public land grant Act of the Federal Congress which was accepted by the General Assembly of the State March 27, 1871, in an act which provided for the location, organization and maintenance of the institution. Fayetteville was selected as the seat, and the University opened January 22, 1872."

From the very beginning there has been a department of chemistry and the science has had a prominent place in the curriculum. T. L. Thompson, B.S., was the Professor of Theoretical and Applied Chemistry as stated in the first catalog. There were ten teachers but only 16 students in the freshman college class, the remainder of the students being either in the normal or preparatory departments. The catalog for 1872–73 shows that two terms of chemistry in the sophomore year were required with the classical course along with Virgil's *Aeneid* and Homer's *Iliad*. In addition to this, students in agriculture studied qualitative analysis in the spring and also the following fall. The engineers



NEW SCIENCE BUILDING, HENDERSON STATE TEACHERS COLLEGE

of that day did not have the qualitative course. That the laboratory was reasonably equipped for so early a date is evidenced by a record under date of February 10, 1874, of "cash paid Professor T. L. Thompson for chemicals—$427.90."

Professor F. L. Harvey, B.S., who succeeded Thompson, reported an estimate in 1875 for chemicals and apparatus of $1500 (*9*).

Originally the chemistry department had recitation rooms and laboratory in the first frame building. Later these were transferred to University Hall which still stands. Then came a chemistry building which has now been destroyed. This was followed in 1905 by a separate building for chemistry, which was transformed into a building for the School of Law when the present building was placed in use in 1935. From the early 1890's there has been a four-year course in chemistry and the number of graduates in chemistry and in chemical engineering now approximates 500.

[6] Second annual catalog, 1887–88, Ouachita Baptist College.
[7] ROBEY, ASHLEY, personal correspondence (1/23/42).

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(9) REYNOLDS AND THOMAS, "History of the University of Arkansas, Fayetteville," University of Arkansas. Fayetteville **1910.**

War Gas Identification Sets

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IN ATTEMPTING to assist those entrusted with the protection of the local civilian population, "sniff sets" of the common war gases have been useful, to acquaint civil defense officials, air wardens, and auxiliary police, with the odors of those gases they are likely to encounter. Fortunately, each gas has its own identifying odor which may be readily recognized by association with common products, but since there is more variation in odor perception than in any other faculty, there will not be complete certainty unless the actual gas is at hand for the identification of its odor.

The purpose of this paper is to offer a means whereby those confronted with the task of training civilian groups may prepare "sniff sets" similar to those used by the military forces. The sets described here were prepared with the facilities of a typical college laboratory. They consist of six glass-stoppered, two-ounce bottles, one each for the following gases: mustard, lewisite, chlorine, chlorpicrin, phosgene, and tear gas (chloracetophenone). Three bottles are half filled with activated charcoal to adsorb the gas. The contents of the other three will be described later. The bottles are placed in holes drilled in a block of wood, to facilitate handling. (See Figure 1.)

It is found advisable to smell the bottles in the following order because of the increasing intensity of the odor: mustard, lewisite, chloracetophenone, chlorine, chlorpicrin, and phosgene. Only enough air should be drawn in to fill the nostrils, as deeper breathing dulls the sense of smell and may prove injurious.

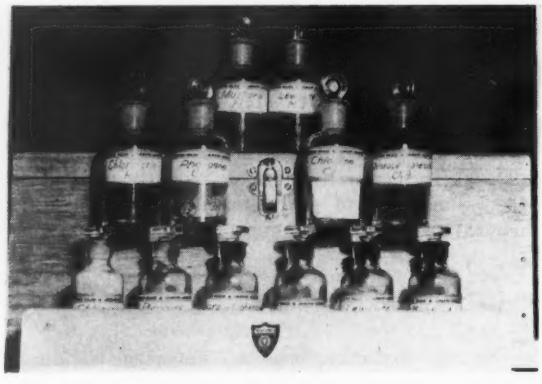

FIGURE 1.—THE "SNIFF SET" FOR IDENTIFICATION OF WAR GASES

In the preparation of these gases caution must of course be observed. A well-ventilated hood, gas masks, and heavy rubber gloves specially made for this purpose are definite requirements. Even these heavy gloves may ultimately be destroyed by lewisite and mustard, and should these liquids be spilled immediate decontamination should be applied. All pieces of apparatus contaminated with persistent agents must be boiled in strong soap solution under the hood for several hours.

MUSTARD GAS (HS)

This gas, β-β'-dichlorethyl sulfide, $(CH_2ClCH_2)_2S$, is a vesicant or blistering agent. It exists in the form of liquid and the vapor has the odor of *mustard*, *horseradish*, or *garlic*. It has a delayed effect, burning the skin or membrane, inflaming the respiratory tract, and thereby leading to pneumonia. Eye irritation and conjunctivitis are other effects noted. Treatment, after removal from the gassed area, consists in undressing the victim, removing liquid mustard with fat solvents such as gasoline, followed by applications of protective ointment or bleaching solution, or baths with strong soap and hot water. The eyes may be treated by irrigation with a two per cent sodium bicarbonate solution.

Chloride of lime reacts slowly with vesicant agents to destroy them. It cannot be applied in the pure form because the reaction is explosive. In order to avoid this the chloride of lime is mixed with earth, one to three parts by weight or two to three parts by volume or shovelful. This mixture, known as Dry Mix, is used to cover ground, roads, etc., with which it must remain in contact for twenty-four hours. Since Dry Mix cannot be applied to walls and ceilings, a slurry is used, made by mixing chloride of lime with water in proportions of one to one by weight or three shovelsful of chloride of lime to two gallons of water.

Clothing can be decontaminated by steaming with live steam for two hours or boiling in water for four hours.

Preparation

Since β-β'-dihydroxyethyl sulfide is commercially available, mustard gas is most conveniently and safely prepared by the method of Gomberg (*1*).

$$(CH_2OHCH_2)_2S + 2HCl \rightarrow (CH_2ClCH_2)_2S + 2H_2O$$

Two hundred and fifty grams of the hydroxy-mustard are dissolved in 400 ml. of concentrated hydrochloric acid and the solution is warmed to 60° to 75°C. until the heavy yellow oil separates as the lower layer. The oil is separated in a separatory funnel and filtered through a layer of calcium chloride or sodium chloride. The product is sufficiently dry for ordinary purposes. If greater purity is desired, the oil may be distilled under reduced pressure and the liquid coming over at 106° to 108°C. at 20 mm. of mercury collected. The distilled product is water white and of such faint odor that it is hardly useful in a "sniff set."

If β-β'-dihydroxyethyl sulfide is not available, mustard gas may be prepared by following Guthrie's (*2*) original method of bubbling ethylene through sulfur monochloride.

$$2C_2H_4 + S_2Cl_2 \rightarrow CH_2ClCH_2SCH_2CH_2Cl + S$$

The reaction takes place in a three-nicked, round-bottomed flask fitted with a dropping funnel, a mechanical stirrer, and an inlet tube for admitting ethylene. (See Figure 2.)

Ethylene is first dried by passing through a tower of concentrated sulfuric acid and one of glass wool, and then admitted to the round-bottomed flask which contains 20 grams of sulfur monochloride introduced through the dropping funnel.[1] During the passage of ethylene, a further 30 grams of sulfur monochloride are added from the funnel. The flask, in a water bath, is heated on an electric hot plate, and a stream of cold water is arranged to flow over the flask in order to maintain a temperature of not over 35°C.

The passage of ethylene is continued until all the sulfur monochloride has been used up. This is determined by treating a little sodium iodide solution on filter paper with a drop of the reaction mixture. A brown stain indicates incomplete reaction.

When reaction is complete, the product is distilled under reduced pressure of 20 mm. (which may be reached with a good filter pump), and the fraction passing over between 106°C. and 108°C. is collected. To avoid a great tendency to bump, a Claissen distilling head is used with a capillary tube admitting a small quantity of air to the bottom of the distilling mixture. The liquid is stored in a glass-stoppered bottle. Interchangeable ground glass joints on all apparatus are a great convenience, because of the ease of decontamination.

About one cubic centimeter of the product is added to the activated charcoal in the "sniff set" bottle.

LEWISITE (M-1)

Lewisite, chlorvinyldichlorarsine, is also a vesicant agent, with an odor unmistakably that of *geraniums*. It penetrates the skin, causing blisters and wounds which heal with difficulty. Arsenical poisoning may also result. Thirty drops on the external skin is sufficient to cause death. Lewisite hydrolyzes readily, but the product of hydrolysis, though poisonous, is not a vesicant. Lewisite persists as liquid or vapor for from one day to one week, or even longer if the weather is cold or dry.

The victim must be undressed and the liquid lewisite removed with hydrogen peroxide, NaOH in glycerin, or kerosene. This is followed by bathing, washing of the eyes and nose with sodium bicarbonate solution. Rest is also essential. Best first aid results are obtained if applied within one or two minutes.

The decontamination treatment for lewisite is the same as that for mustard gas.

[1] The preparation of sulfur monochloride, by direct combination of chlorine with melted sulfur, is described in most manuals of inorganic preparations.

Preparation

It is prepared by condensing arsenic trichloride with acetylene in the presence of anhydrous aluminum chloride (*3*).

$$C_2H_2 + AsCl_3 \rightarrow ClCH{=}CHAsCl_2$$

The apparatus used is similar to that used in the preparation of mustard gas except for the elimination of the dropping funnel.

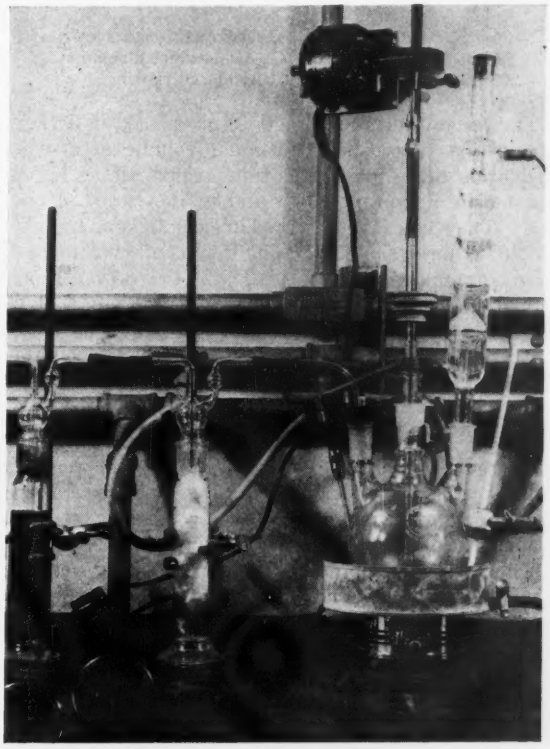

FIGURE 2.—APPARATUS FOR SYNTHESIS OF MUSTARD GAS

Forty-five grams of arsenic trichloride and 15 grams of anhydrous aluminum chloride are placed in the three-necked, round-bottomed flask, fitted as before with a mechanical stirrer and an inlet tube for the admission of acetylene. The flask is constantly cooled by allowing water to flow over the surface.

While stirring, six to eight liters of acetylene, first dried by passing through a sulfuric acid wash bottle and a tower containing glass wool, are bubbled in at the rate of three bubbles per second for about two hours. The reaction is accompanied by the evolution of heat, and the mixture must be cooled in order to maintain a temperature of from 30° to 35°C. Higher temperatures may result in a violent explosion.

When the acetylene has been added, the reaction mixture is poured slowly (*Caution!*) into 200 ml. of 20 per cent hydrochloric acid (about 55 per cent concentrated hydrochloric acid and 45 per cent water) cooled to about 0°C. The mixture is distilled in a steam dis-

tillation apparatus, but with constant boiling hydrochloric acid substituted for the water in the steam generator. This technique avoids the violent explosion which usually occurs if the oily layer of the reaction mixture is distilled directly (*4*).

The oily layer is fractionally distilled at reduced pressure (20 mm. to 30 mm.) until 90°C. is reached. Receivers are changed and the distillation is continued to 105°C. This is the lewisite fraction.

The fractionation temperatures are as follows:

First fraction, 90°–105°C., chlorvinyldichlorarsine
Second fraction, 125°–140°C., dichlorvinylchlorarsine
Third fraction, 145°–160°C., trichlorvinylarsine

The second and third fractions are placed in a glass combustion tube, about an equal volume of arsenic trichloride added, and the tube sealed off. This is inserted in an iron pipe of suitable size, closed at one end. The whole is then heated in a combustion furnace at 210°C. for four hours. The tube is allowed to cool to room temperature, opened, and the contents are refractionated. An additional yield of lewisite is thus obtained.

About one-half cubic centimeter of lewisite on the activated charcoal is sufficient for the sniff bottle.

PHOSGENE (CG)

Phosgene (carbonyl chloride), $COCl_2$, is a lung irritant with the odor of *fresh cut corn* or *musty hay*. It produces irritation of the lungs, occasional vomiting, tears in the eyes, and a "doped" feeling.

The appearance of the symptoms may be delayed for six hours. Extreme exposure may result in collapse and heart failure. The victim must be kept warm and given absolute rest and non-alcoholic stimulants. The gas will persist for from ten to thirty minutes.

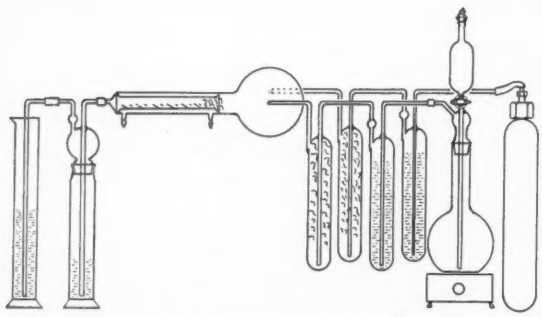

FIGURE 3.—APPARATUS FOR SYNTHESIS OF PHOSGENE

Preparation

Phosgene is prepared by the reaction of carbon monoxide and chlorine in the presence of activated charcoal as a catalyst (*5*).

$$CO + Cl_2 \rightarrow COCl_2$$

Carbon monoxide is prepared by dropping formic acid upon hot concentrated sulfuric acid, the flask being heated to 100°C. on an electric hot plate. The carbon monoxide thus prepared, and chlorine from a gas lecture bottle or other source, are each led through two wash bottles, the first containing concentrated sulfuric acid and the second glass wool. The purified gases are admitted to a round-bottomed flask for mixing. (See Figure 3.)

The mixture is then passed through a condenser tube containing activated charcoal to catalyze the combination to phosgene. The literature suggests a water-cooled outer jacket to control an exothermic reaction but best results were obtained by passing steam and not cold water through this outer jacket.

The phosgene emerging from the condenser is dissolved in about 100 ml. of benzene and is used in this form in the "sniff set." Since activated charcoal appears to hydrolyze the phosgene to hydrogen chloride, it is necessary to substitute another absorbent. The bottle for the set is half filled with a magnesia-asbestos mixture (material used for packing dangerous chemicals), and this is saturated with the solution of phosgene in benzene. This mixture has proved very satisfactory and the odor from it has remained characteristic and strong for over a month in constant use.

It was found necessary to make the apparatus all of glass because of the tendency of the gases to leak through rubber connections.

CHLORINE (CL)

This gas is classified as a lung irritant with a *highly pungent* odor. One exposed to this gas must be removed from the area and kept quiet and warm. The gas persists for about ten minutes.

Preparation

This should present very little difficulty, as the usual methods of laboratory preparation may be used. However, for purposes of "sniff sets" high test (HTH) chloride of lime (calcium hypochlorite, available chlorine not less than 70 per cent) is used. The small glass-stoppered bottle is about half filled with this solid and offers sufficient odor for detection.

HTH serves also to illustrate the danger of applying pure chloride of lime to mustard gas. The demonstration is safely carried out by placing 5 ml. of ethylene glycol in a porcelain dish and sprinkling 5 grams of HTH over the surface. The resulting flame and explosion are quite similar to those caused by adding pure chloride of lime to mustard gas.

CHLORPICRIN (PS)

Chlorpicrin, CCl_3NO_2, is a colorless oily liquid with the odor of *flypaper, anise,* or a *smoldering rag*. It is primarily a lung irritant and secondarily a lacrimator which causes severe coughing, crying, and vomiting. Washing of the eyes, quiet, and warmth are recommended as treatment for one exposed to this gas. Although chlorpicrin is ordinarily classified as

a non-persistent agent (*i. e.*, less than ten minutes) the literature gives longer periods of from one hour to one week, depending upon weather conditions and location. For this reason decontamination by sodium sulfite in alcohol might be necessary in certain cases.

Preparation

Chlorpicrin is prepared by the method proposed by Hoffmann (*6*).

$$C_6H_2(NO_2)_3OH + 11Cl_2 + 5H_2O \rightarrow 3CCl_3NO_2 + 13HCl + 3CO_2$$

Five hundred fifty grams of chloride of lime (about 30 per cent available chlorine) are made into a paste by the addition of about a liter of water. This is placed in a five-liter, round-bottomed flask, fitted with a two-holed rubber stopper. A paste of sodium picrate is then prepared by mixing 50 grams of picric acid, 10 grams of sodium hydroxide, and 250 ml. of water. The sodium picrate is added to the chloride of lime in the flask with continuous stirring. The reaction takes place very rapidly and is completed in about one-half hour. The flask is connected to a condenser and the contents steam distilled until no more oily droplets come over. A sodium sulfite trap is attached to the receiver to eliminate fumes. Care must be taken to avoid calcium hydroxide frothing over.

The oily distillate is removed in a separatory funnel, dried over calcium chloride, and redistilled; chlorpicrin boils off at 112°C.

About one cubic centimeter of chlorpicrin is added to the activated charcoal of the "sniff bottle."

CHLORACETOPHENONE (CN)

This agent, $C_6H_5COCH_2Cl$, is a lacrimator, *i. e.*, a substance having a specific action on the eyes and producing a copious flow of tears and temporary blindness. It is a solid with the sweet odor of *locust* or *apple blossoms*. Chloracetophenone is usually disseminated as a smoke. First aid treatment consists of washing the eyes of the victim with cold water or boric acid solution. For the skin, sodium bicarbonate solution is suggested. The gas will persist for about ten minutes.

Preparation

Chloracetophenone is best prepared by the following method:

$$CH_2ClCOCl + C_6H_6 \rightarrow C_6H_5COCH_2Cl + HCl$$

In the usual Friedel-Crafts procedure, 55 grams of anhydrous powdered aluminum chloride are added to 100 cc. of thiophene-free, dry benzene. Forty-five grams (30 cc.) of chloracetylchloride are added slowly over a half-hour period with shaking, followed by refluxing for another half hour on a water bath. After cooling, the reaction mixture is slowly poured over a mixture of 150 grams of ice and 150 grams of concentrated hydrochloric acid. In order to obtain a clear water layer it may be necessary to add a small amount of water or of hydrochloric acid. Thirty cc. of ether are added and the whole shaken in a separatory funnel.

The oily layer is washed again with water and then dried over calcium chloride. Ether and benzene are removed by distillation on a steam bath which is then replaced by a Bunsen burner; the temperature is cautiously raised to 150°C. An air condenser is now substituted and the distillation continued. Chloracetophenone will distil from 235° to 255°C. The oily distillate is poured into ice water and the crystals are collected and dried on a Büchner funnel. If greater purity is desired these may be recrystallized from alcohol.

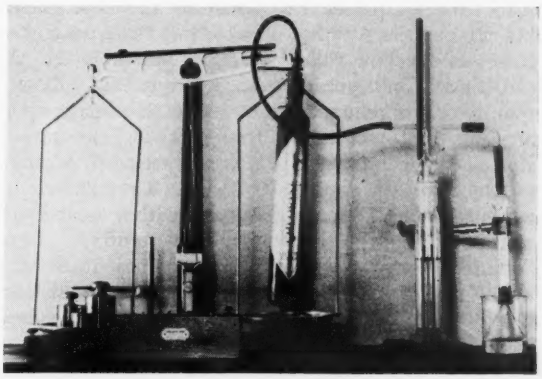

FIGURE 4.—CHLORINATION OF ACETOPHENONE

Second Procedure

Because of the possible difficulty of obtaining chloracetylchloride, the method of Kirten and Scholl (*7*) is also included here.

$$C_6H_5COCH_3 + Cl_2 \rightarrow C_6H_5COCH_2Cl + HCl$$

The acetophenone is prepared by the Friedel-Crafts reaction as described in any organic chemistry laboratory manual.

Fifteen grams of redistilled acetophenone are dissolved in 100 grams of glacial acetic acid and the solution is introduced into a tall gas wash bottle which is fitted with an inverted funnel attached to the delivery tube. The funnel is placed in a beaker of water in such a way that the lower edge comes to a quarter of an inch above the water surface. From a chlorine lecture bottle, tared on a balance and connected to the gas wash bottle by flexible rubber tubing, 8.9 grams of chlorine are introduced into the wash bottle and an ultra-violet light is directed on the reaction mixture. Sunlight will serve the same purpose. (See Figure 4.)

After about ten minutes the solution becomes colorless and reaction is complete at this point. The reaction mixture is then poured into 500 cc. of water-ice mixture and the chloracetophenone immediately solidifies. In order to free the solid from the oily material, the mixture is poured into a Büchner filter. After drying for some time in the funnel, the crystals will be

found to retain some of the oily material which can, if desired, be removed by dissolving the crystals in pure alcohol and recrystallizing from a 50 per cent water-alcohol solution.

Since a solution of CN has only the odor of the solvent the crystals themselves are placed in the bottle for the "sniff set."

ADAMSITE (DM)

Adamsite, diphenylaminechlorarsine, is classed as a sternutator. Like chloracetophenone, it is disseminated as a smoke which, because of the small size of its particles, passes through all but the most efficient gas mask filters. It has no odor but the smoke cloud possesses a yellow color. Adamsite irritates the nose and throat and produces successively the following symptoms: coughing and sneezing, lacrimation, depression, and vomiting. Though the symptoms are almost immediate and extremely severe, complete recovery follows in three to twelve hours. First aid measures include spraying the nose with a one per cent ephedrine solution in water, salt solution, or oil. Sodium bicarbonate (two per cent) may be used to wash the throat. Aspirin may be administered. Contaminated clothes should be removed and the body bathed to remove adhering particles.

Since adamsite has no odor it was not thought necessary to include it in a "sniff set." But since it is the chief harassing agent of the army, directions for its synthesis are included.

Preparation

A convenient laboratory method, suggested by Contardi (*8*) is the treatment of diphenylamine hydrochloride with arsenious oxide.

$$2(C_6H_5)_2NH\cdot HCl + As_2O_3 \rightarrow 2NH(C_6H_4)_2AsCl + 3H_2O$$

Diphenylamine hydrochloride is prepared by treating 40 grams of diphenylamine with 20 ml. of HCl (sp. gr. 1.19) in a large porcelain dish. The mixture is heated with constant stirring until all the water is driven off. The resulting white powder is dried for two or three hours at 50° to 60°C., after which 24 grams of arsenious oxide are added and the mixture heated with constant stirring until the melting point is reached. The temperature is gradually raised and at 140°C. reaction becomes vigorous with the evolution of water vapor. After three or four hours, the temperature reaches 200°C. and no more water vapor comes off. The mixture is allowed to cool, is extracted with xylene, and bright yellow crystals are recovered by recrystallization.

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CHEMICAL WARFARE[1]

Methods of Gas Identification—Gas-Proof Shelters[2]

IN ADDITION to sensory methods, chemical reagents which are very sensitive, and several of which are specific, may be used in identification of gases.

Of the reagents mentioned, all, except the solutions of auric chloride in water and hydrogen sulfide in acetone, are used under the form of reactive papers which are prepared either in advance or at the moment of usage by impregnation of white filter-paper bands which are then allowed to drain. If the reactive paper has been prepared in advance, it should be moistened before using. The five following reagents are best known:

(1) *Baubigny or fluorescein reagent:*

It characterizes *chlorine* and *bromine*. The color of the reagent turns from greenish yellow to pink owing to formation of eosin or tetrabromfluorescein. The reagent is made of the following constituents:

Fluorescein	0.20 g.
Potassium bromide	30 g.
Potassium carbonate	2 g.
KOH, 10%	2 cc.
Glycerin	1 g.
Distilled water	Up to 100 cc.

(2) *Harrison reagent:*

It is specific of *phosgene*. The color of the reagent turns from light yellow to yellow, orange or brown, according to concentration. Its constituents are the following:

Para-dimethylaminobenzaldehyde	1 g.
Diphenylamine	1 g.
Alcohol, 95%	20 cc.

(3) *Cupric-benzidine acetate reagent:*

It characterizes *prussic acid* (in absence of chlorine). The color of the reagent turns to blue. It comprises two solutions which are mixed together in equal volumes before using.

The two solutions are made as follows:

[1] Reprinted with the permission of the editor from *Canadian Chemistry and Process Industries*, May, 1942, p. 272.
[2] Sections of a paper prepared by C. E. Beland, F.C.I.C.

Solution I:

Cupric acetate	2.80 g.
Acetic acid	2 g.
Distilled water	1000 cc.

Solution II:

Saturated aqueous solution of benzidine acetate	475 cc.
Acetic acid	2 g.
Distilled water	525 cc.

(4) *Schroter reagent:*

It identifies *mustard gas* (in absence of carbon monoxide and hydrogen sulfide) by formation of a precipitate. It is prepared as follows:

Auric chloride	1 g.
Hydrochloric acid	1 g.
Distilled water	1000 cc.

(5) *Peronnet reagent:*

It is specific of *Lewisite*. It consists of hydrogen sulfide dissolved in acetone, and the indication is a bright yellow precipitate.

GAS-PROOF SHELTERS

Gas-proof shelters are constructed in such a way as to prevent contaminated air from entering, or to filter noxious gases from the air which enters. It is not necessary to wear gas masks when in them. The shelters are required as places in which to eat, sleep, and rest when the gas attack is prolonged or when the enemy uses a persistent agent. They are also desirable for medical or telephonic services, in which the wearing of a mask would be an embarrassment. Distinction is made between unventilated and ventilated shelters.

Unventilated shelters consist of buildings, rooms, or cellars hermetically sealed so as to prevent outside air from entering. They can be utilized only for a limited length of time, because the air contained in them becomes vitiated; this time depends on the size of the apartment and the number of occupants.

In constructing an unventilated shelter, a floor space of 20 square feet is allowed per person. If the ceiling be at a height of 8 to 10 feet, the people sheltered have air sufficient for 10 hours. An apartment of 10 feet by 10 feet will accommodate 5 persons; one of 20 feet by 12 feet, 12 persons.

The walls and ceiling should be made of concrete at least 12 inches thick, and should not be covered with steel because this would affect the absorption of carbon dioxide. It is estimated that, if the shelter be occupied by adults of an average weight of 160 pounds, it will become unfit for use at the end of 10 hours when the carbon dioxide content will have attained the permissible limit of 2 per cent. After this time, the excess of carbon dioxide provokes difficulty in breathing, headaches, vomiting and even loss of consciousness. The rising temperature (about 10 degrees every 8 hours) and the lack of air circulation add to the troubles of the occupants; so, the utilization of an electric fan and of bags filled with active charcoal and soda lime is advantageous.

Ventilated shelters are such quarters as may be occupied indefinitely for protection against gas. Air entering is first purified by filtration. If the gas shelter is to be used during 10 hours, or if each occupant be obliged to occupy lesser space than 20 square feet of floor space, mechanical ventilation will be required. In order to not exceed the limit of 2 per cent of carbon dioxide, each person must be provided with 33 cubic feet of air per hour. The apparatus for this consists of one or more large suction filter intakes, operated by hand or by a motor. Each one of these permits the aspiration of 80 cubic feet of air per minute using $^1/_{10}$ horsepower, with a resistance equal to that of a 4-inch water-column, this supplying a minimum of $1^1/_2$ cubic feet of air per minute for 52 people. It will be necessary to employ two or three filter breathers, according as the number of occupants varies between 52 and 105, or from 105 to 157.

This apparatus permits not only the intake of the required air, but also its purification by absorbing the toxic gases and fumes in the same manner as the gas masks. It is desirable that ventilated shelters be equipped with two air intakes, placed as high as possible above the ground, because the gases are heavier than air. In cold weather, the air must be heated to 60°F.; in warm weather, the air must be cooled because the amount brought in is insufficient to remove more than a fraction of the heat emitted by the human beings and the lighting.

CIVILIAN USE OF GAS MASKS

"THE cry now going up for civilian gas masks, if heeded, will result in a crime of the first magnitude against our offense effort," Joel H. Hildebrand, chairman of the Department of Chemistry, University of California, and co-designer of the American Army gas mask of 1918, said in addressing the Commonwealth Club of California in San Francisco, March 6.

Continuing, Dr. Hildebrand said:

"Unless you are some sort of warden, you have little excuse for being exposed to toxic gas. You should stay indoors, where you are better protected without a gas mask than you would be out-of-doors with one.

"Close all doors and windows and shut off any furnace that draws air in from the outside. Seal the cracks, if you are very nervous, with tape or wet rags or paper. Go to the upper floors and wait for the gas to blow away or for the street squads to disinfect. Breathe through a wet towel, and, if this is not sufficient comfort, put your head under a pillow and pray.

"You do not need a gas mask and you are disloyal to our fighters if you demand one when labor, rubber, and other materials are so vitally needed for fighting purposes."

—From *Chemical and Engineering News*, **20,** 412 (March 25, 1942)

The Apparent Degree of Ionization of Hydrochloric, Sulfuric, and Acetic Acids

An Electrolytic Conductivity Experiment for General Chemistry

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Oregon State College, Corvallis, Oregon

IN PRESENTING the theories of ionization in general chemistry, the qualitative demonstration of conductivity using a light bulb leaves much to be desired in a comparison of electrolytes generally classed as "good" or "fair" conductors. The need for a quantitative experiment is met in this paper, which describes an adaptation of the conductivity bridge experiments performed in physical chemistry, and measures the conductivities of various electrolytes over wide ranges of concentration. A simple conductivity cell with adjustable electrodes allows the current, in amperes, to be numerically equal to the "effective" ionic concentration of the electrolyte. With this simple conversion factor of unity the effective ionic concentration is then expressed in percentage as the apparent degree of ionization.

The apparent degrees of ionization of hydrochloric, of sulfuric, and of acetic acid are determined at various concentrations up to 10 molar. In the case of acetic acid a factor of ten is introduced for converting conductivity, expressed in amperes, into the effective ionic concentration.

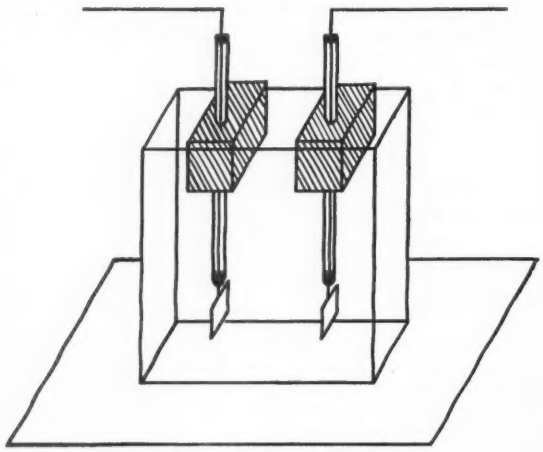

FIGURE 1.—CONDUCTIVITY CELL

APPARATUS

A 2 cm. by 7.5 cm. by 7.5 cm. conductivity cell (Figure 1) was constructed by cementing together ordinary glass plates. The platinum electrodes, 1 cm. by 2.25 cm., were sealed in glass tubing and held in place by sections of cork. The electrodes were blackened by electrolyzing a dilute solution of chloroplatinic acid. Shiny platinum electrodes are less satisfactory.

TABLE 1

APPARENT DEGREE OF IONIZATION OF HYDROCHLORIC ACID AT 25°C.

Concentration of HCl (Molarity)	*Electrolytic Conductivity (Amperes)*	*Apparent Degree of Ionization (Per Cent)*
0.001	0.001	100
0.01	0.0097	97
0.1	0.092	92
0.5	0.42	84
1.0	0.80	80
2.5	1.60	64
5.0	2.10	42
7.0	2.12	30.3
10.0	1.82	18.2

The conductivity cell, a current meter, and a tapping key were connected in series with from two to six cells of a storage battery, the number of cells depending upon the acid employed. Three milliammeters with scales 0–5, 0–30, 0–250, and an ammeter with scales 0–0.5 and 0–5 amperes were employed. In the three electrolytes described in this paper the milliammeter of 0–5 scale, each scale division equal to 0.1 milliampere, was satisfactory for measuring the conductivity of the most dilute solutions. The results are more consistent when a minimum number of current meters is used for a series of measurements, since the internal resistances of the different meters may vary.

PROCEDURE

Hydrochloric Acid

Solutions of various concentrations (Table 1) from 10 *M* to 0.001 *M* are prepared by successive dilutions of 12 *M* hydrochloric acid. Fifty milliliters of 0.01 *M* acid are placed in the cell. The same volume of solution is used for later tests. The cell is connected in series with two cells of a storage battery, a milliammeter which covers the 10 milliampere range, and a tapping key. The key is depressed for a few minutes or until the milliammeter gives a constant reading. The electrodes are then adjusted so that the current is 9.7 milliamperes. This value is chosen since it, 0.0097 ampere, is numerically equal to the effective ionic concentration of 0.01 *M* acid (obtained from data[1] showing

[1] ENGELDER, "Elementary qualitative analysis," John Wiley and Sons, Inc., New York City, 1933, p. 7.

that 0.01 *M* hydrochloric acid has an apparent degree of ionization of 97 per cent).

It is desirable that this initial adjustment of the electrodes for the entire series of solutions be based upon a solution which approaches 100 per cent apparent degree of ionization. Solutions more dilute than 0.01 *M* are less satisfactory because too much time is required for constant readings.

TABLE 2

APPARENT DEGREE OF IONIZATION OF SULFURIC ACID AT 25°C.

Concentration of H_2SO_4 (Molarity)	*Electrolytic Conductivity (Amperes)*	*Apparent Degree of Ionization (Per Cent)*
0.0001	0.0001	100
0.001	0.00095	95
0.01	0.009	90
0.05	0.032	64
0.1	0.060	60
0.2	0.114	57
0.5	0.272	54
1.0	0.50	50
2.5	0.88	35.2
5.0	0.98	19.6
7.0	0.72	10.3
10.0	0.380	3.80

With the electrodes in this fixed position the cell is emptied and rinsed with the next solution of hydrochloric acid to be tested and then filled with the same volume as before. Solutions of the various concentrations are made up far enough in advance so they are all at the same temperature when tested. A milliammeter of appropriate range is placed in the circuit and the current measurements in the series, as in Table 1, are numerically equal to the effective ionic concentration of the acid.

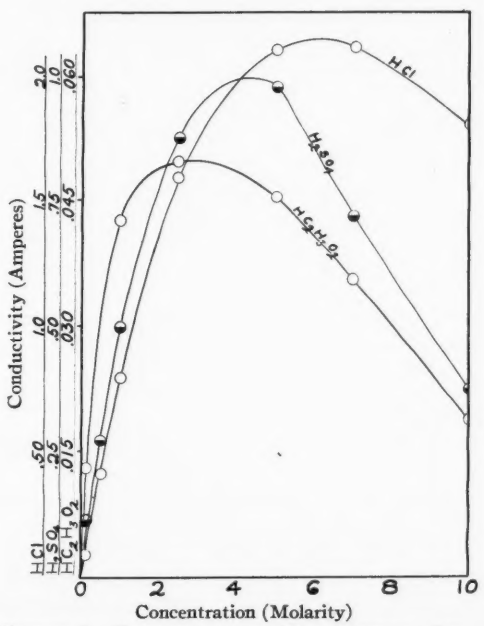

FIGURE 2.—CONDUCTIVITY OF HYDROCHLORIC, SULFURIC, AND ACETIC ACIDS AT 25°C.

The apparent degree of ionization is calculated from the corresponding molar concentrations and conductivity data. For example, the conductivity of 0.5 *M* acid is 0.42 ampere. The apparent degree of ionization is

$$\frac{(0.42 \times 100)}{0.5} = 84\%$$

In the more concentrated solutions the tapping key is depressed only long enough to observe the current reading. Continued passage of large currents removes the black coating on the electrodes.

The data from Table 1 are plotted in Figures 2 and 3.

Sulfuric Acid

The conductivity of sulfuric acid at various concentrations is measured in a manner similar to that used for hydrochloric acid. Using 4 volts potential and 36 ml. of 0.05 *M* solution the electrodes are adjusted so that 32 milliamperes pass at 25°C. In the literature[2] the apparent ionization of 0.1 *N* H_2SO_4 is 59 per cent at 18°C. Since the data are not given for 25°C., the following method was used to obtain this value. The electrodes were adjusted so that 0.0295 ampere passed through the cell at 18°C. The temperature was raised to 25°C., and the current reading was observed to be 0.032 ampere. This corresponds to an ionization value of 64 per cent.

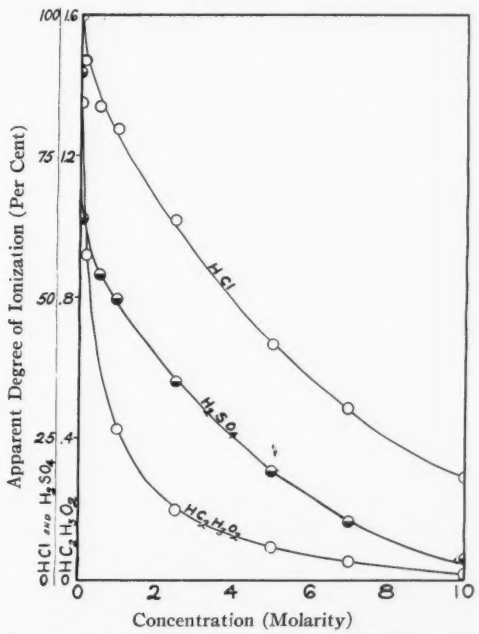

FIGURE 3.—APPARENT DEGREE OF IONIZATION OF HYDROCHLORIC, SULFURIC, AND ACETIC ACIDS AT 25°C.

Other concentrations of the acid are tested with the

[2] ANDERSON AND HAZLEHURST, "Qualitative analysis," Prentice-Hall, Inc., New York City, 1941, p. 251.

same setting of electrodes. See Table 2 and Figures 2 and 3.

Acetic Acid

Since acetic acid is a weak electrolyte it is not feasible to move the electrodes close enough together or to use enough voltage to make the conductivity when expressed in amperes to be numerically equal to the effective ionic concentration. However, it is possible to introduce a factor of ten to relate the two quantities.

A 0.1 *M* solution is chosen as the reference solution. This solution has an apparent degree of ionization of 1.35 per cent at 25°C.[3] Using the technic described above, it is found that by using 12 volts potential the electrodes can be adjusted so that the current is 13.5 milliamperes. See Table 3 and Figures 2 and 3.

[3] MACINNES AND SHEDLOVSKY, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

The substitution of this quantitative experiment as a lecture demonstration in the authors' classes has aroused more interest than the student performance of the usual qualitative, light-bulb conductivity experiment. After the data are collected, the students plot the curves and interpret them.

TABLE 3

APPARENT DEGREE OF IONIZATION OF ACETIC ACID AT 25°C.

Concentration of Acetic Acid (Molarity)	*Electrolytic Conductivity* $\left(\frac{Amperes}{10}\right)$	*Apparent Degree of Ionization (Per Cent)*
0.0001	0.000041	41
0.001	0.000126	12.6
0.01	0.00045	4.5
0.05	0.00095	1.90
0.1	0.00135	1.35
0.2	0.00185	0.925
1.0	0.0043	0.43
2.5	0.0050	0.20
5.0	0.0046	0.092
7.0	0.0036	0.051
10.0	0.0019	0.19

AN ALKALINE CLEANING SOLUTION

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THE problem of cleaning glassware in the chemistry laboratory has been neglected in many schools. While it is true that the student in quantitative analysis is given a bottle of chromic acid cleaner, the struggling freshman has been given a test-tube brush and our best wishes. To solve this problem we have tried a number of mixtures of detergents, and to our mind the following procedure is to be recommended:

At strategic points, determined by a study of the traffic flow in the freshman laboratory, there are placed small enamel dishpans containing about two quarts of a detergent solution. Under each pan are a Bunsen burner and a micro burner. The solution is heated to 70°C. with the Bunsen and maintained at that temperature with the micro burner. Usually the most convenient location for the cleaning unit will be the hood, since it is usually equipped with the gas outlets.

If the water in the laboratory is unusually hard, it is advisable after the cleaning to rinse the glassware in soft water. For this purpose there should be provided beside the hot detergent solution a large dishpan full of soft water. A homemade zeolite softener can be made by placing five pounds of zeolite in a gallon jar.

The cleaning mixture has been empirically formulated by actual experience. Since the problem in cleaning glassware is to cut the film of grease, the detergent is mixed with the usual alkaline detergents of TSP, TSPP, and Metso as the principal ingredients. To give a good suds Dreft is added. To inactivate the alkaline earth ions Calgon is used. Finally, to reduce the surface tension a wetting agent of the alkyl aryl sulfonate type is added.

2¾	pounds of Calgon	$1.00
1	pound of wetting agent	0.60
10	pounds of sodium metasilicate	0.50
12	pounds of tetrasodium pyrophosphate	0.70
36	pounds of trisodium phosphate	1.50
1	pound of Dreft	0.40

Thus a total of 63 pounds of the detergent costs $4.70. Since only one ounce of the detergent is added to two liters of water for use in the laboratory, it is apparent that the cost of the detergent is of no consequence when compared to the cost of the chromic acid cleaner.

The alkaline detergents have proved so satisfactory, compared to chromic acid, that they are used in all our laboratories. In quantitative analysis the beakers, flasks, and burets come out of a one-minute soak in hot detergent free from all grease. A rinse with soft water and then distilled water leaves them sparkling. In the organic laboratory the hot alkaline detergent is especially useful in cleaning partially carbonized residues out of distilling flasks.

Other advantages of the use of an alkaline detergent are:

1. The use of hot chromic acid cleaner is a potential accident hazard.

2. The storeroom inventory of test-tube brushes can be greatly reduced. Brushes need not be issued to individual lockers. A brush is always left at the pan of the hot detergent solution.

3. It has always seemed an anomalous teaching practice to spend a period of lecture time extolling the virtues of the newer types of detergents and to ignore their practical application in the laboratory. Here is an opportunity to do a realistic teaching job by making available a really efficient cleaning aid.

Lantern Slides of Actual Crystals

HARRIETT H. FILLINGER *Hollins College, Hollins, Virginia*

THROUGH an accidental crystallization in the laboratory some time ago it occurred to the writer that crystals might be grown on lantern-slide cover glasses and mounted into permanent slides. This problem was presented last year to Miss Warren Williamson, a senior chemistry major, who was registered for a small piece of rather independent work. To her should go the major portion of the credit for the successful execution of the idea. She suggested some of the technics and developed the skills necessary to the preparation of the more or less permanent lantern slides herein reported. Since this preliminary work has proved promising in its results and its usefulness for demonstration in elementary courses and since it is a problem which is adapted to undergraduate work, we expect to press the study somewhat further and to improve the technics at certain points. Therefore, this report[1] should be considered in the nature of a progress report.

FIGURE 1.—CUPRIC SULFATE

The slides shown in the illustrations, which are photographs of the enlarged images of the slides on a screen, are among the several dozen which to date have proved to be most successful. In the selection of chemicals for this work, certain obvious characteristics such as the solubility of the compound, the bulkiness of its crystals, its stability under light and moderate heat, possible efflorescence, and deliquescence must be considered. For instance, a chemical such as cupric nitrate which gave beautiful slides was found to be entirely too deliquescent for anything other than very temporary use. But, if handled properly, sometimes surprisingly bulky crystals such as cupric sulfate gave good results. Probably no rule can be laid down for the selection of materials to be used. The three-dimensional difficulties involved in showing the crystals, even those such as cupric sulfate, were easily overcome by changing the focus of the lantern during the showing of the slide. The importance of making slight changes in the focus of the lantern for some slides is illustrated in the photograph in Figure 1. This slide of cupric sulfate is by no means the best slide obtained, but it is mentioned at this point because, on first thought, it would seem to offer much less chance of success than such substances as thiourea or benzoic acid (Figure 2). Because of the rapid growth of cupric chloride in clusters, it does not show up so well in a photograph,

FIGURE 2.—BENZOIC ACID

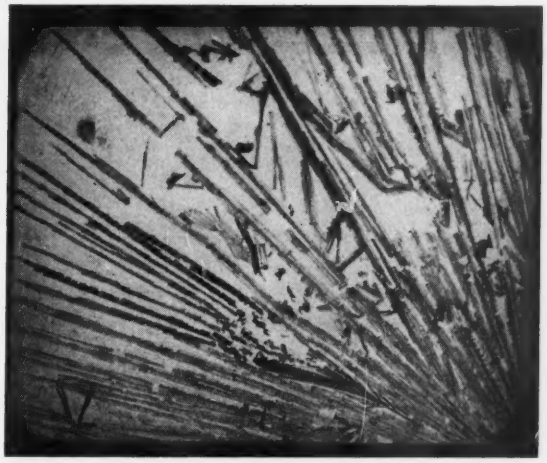

FIGURE 3.—OXALIC ACID

[1] Also presented before the nineteenth annual meeting of the Virginia Academy of Science, Richmond, Virginia, May 2, 1941.

but does become very successful and interesting in the lantern. Such compounds as potassium ferricyanide, mercuric chloride, and oxalic acid (Figure 3), if handled properly, were found to be well adapted to our purpose

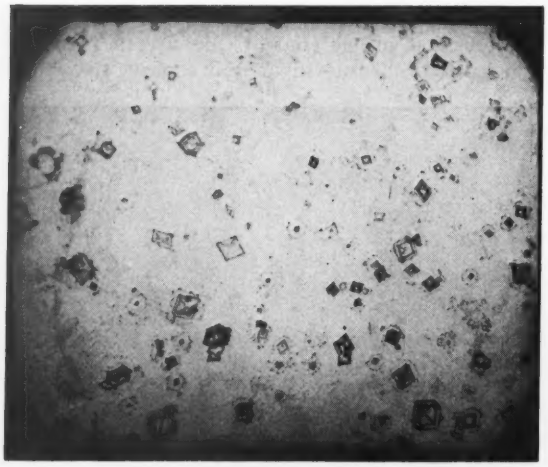

FIGURE 4.—POTASSIUM CHLORATE

and yielded very fine slides which are in good condition after nearly a year of handling and use. The potassium chlorate slide (Figure 4) is of interest in showing the "corner effects" brought about, no doubt, by interruptions in the growth of the crystals. These effects probably resulted from partial dissolvings due to slight temperature changes during crystallization.

Several more or less successful attempts were made to make slides by growing crystals from a supersaturated solution in a very thin cell made by a method described in a former issue of this JOURNAL.[2] A slide

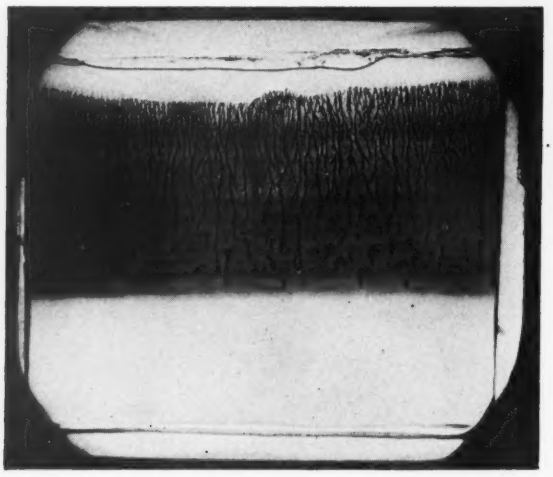

FIGURE 5.—BASIC MERCURIC CHLORIDE IN SILICA GEL

of sodium acetate was made in this way. Slides illustrating rhythmic banding and "metal tree" growth in silicic acid gel were attempted with successful results. Figures 5 and 6 of basic mercuric chloride and a "lead tree" represent beautiful slides which after nine or ten months are in very good condition. No wholly successful method of sealing these cells has been found; at present they are kept standing in water. A number of these cells placed in a desiccator containing water are in fairly good condition after ten months of such treatment. It may be stated here parenthetically that some of the slides made by precipitation in gel which were too opaque to be of use in the lantern were even more beautiful examples of rhythmic banding than those formed by precipitations of the gel in a test tube. They suggest some interesting departures in technic for colloid chemists interested in rhythmic precipitation.

In the preparation of these slides no one technic proved equally successful in every case, but the several

FIGURE 6.—LEAD TREES

methods which seemed most useful will be mentioned. The most successful one was that used in making all but two of the slides here illustrated. Clean cover glasses were immersed in saturated solutions which were allowed to evaporate very slowly, thus making the crystallization from the solution take place at a slow rate. An inexpensive glass pie plate with a second plate inverted over it as a cover proved to be very satisfactory apparatus for the work. By sliding the top pie plate a bit to one side or lifting it with a match stick or other wedge nearly any desired rate of evaporation could be obtained. The slides were examined often after crystallization began to take place. Obviously, it was important to remove the cover glass from the solution at the right time. This required some skill and good judgment based on experience in working with the materials. Before the crystal growth on the glass had become too thick the cover glass was carefully lifted from the solution and drained as quickly as possible in an upright position. Such thin films of

[2] CONWAY, J. CHEM. EDUC., **16**, 314 (1939).

solution which did not drain off the slide fairly rapidly evaporated and were responsible for minute crystals which were termed "trash." Various methods of removing the solution adhering to the glass were tried, but, to date, the drainage method has given best results. However, such "trash" frequently appears, does not interfere in any way with the usefulness of the slides and often, by showing the general "structure of the growth" of the crystals, enhances the appearance of the slide. In using this method it was found that best results were obtained sometimes by having the slide barely covered with the saturated solution during crystallization, and at other times best results were obtained by having the surface of the cover glass a half centimeter or more beneath the surface of the saturated solution. Here, again, it is not possible to lay down any rule. Compounds whose saturated solutions were reasonably dilute were found, in most cases, to yield the best results. For the reason just mentioned water solutions of organic compounds which yielded extremely dilute saturated solutions were found to give better results than solutions of these compounds in organic solvents.

To show what might be called the general structure of the growth of the crystals a second technic proved effective. One large drop or several smaller drops of the saturated solution were placed on the cover glass and allowed to evaporate quickly at room temperature or at temperatures somewhat above that of the room.

The crystals grew from the circumference toward the center of the drop and produced many beautiful effects which are well adapted to use with the lantern.

A third technic was found possible in some cases, but yielded slides with what might be called an artificial appearance. It was found possible to lift from the solution rather bulky crystals such as those of cupric sulfate and the long, sturdy crystals of potassium ferricyanide and place them on a clean cover glass. The solution adhering to the crystal, in most cases, was sufficient to cement it to the glass. The fourth method of using a cell and supersaturated solution, as previously mentioned, gave some beautiful effects, but for obvious reasons was not considered a satisfactory method for making permanent lantern slides of actual crystals.

The mounting of the slides after they were clean and dry was a fairly simple matter. Drops of Duco or some such cement were put at the corners of the slide and sometimes at the center of the long edge and allowed to set in order to support the upper cover glass and allow it just to touch the crystals but not to rest upon them. The two cover glasses with the crystals between them were bound together with ordinary black binding tape, thus yielding a lantern slide which fits into the slide-carriage of an ordinary lantern.

At the present time a student is experimenting with the use of two pieces of polaroid in connection with these lantern slides of crystals. It is hoped that some interesting demonstrations may result.

A SIMPLIFIED DERIVATION OF THE BOHR ATOM

LESTER S. GUSS

South Dakota State College, Brookings, South Dakota

IN THE derivation of the Bohr theory of the hydrogen atom, textbooks in physical chemistry refer to the quantizing condition of Bohr that the angular momentum of the electron must be an integral multiple of $h/2\pi$.

Most students in physical chemistry, however, fail to realize the true significance of the units of rotational motion. It seems, therefore, that a derivation based on units of linear motion would be preferred in the elementary course. In doing this, it is necessary to consider the electrons in the same sense as Planck did the linear oscillator, that the phase integral $\oint pdq$ is a multiple integral of h. Since the integral must extend over a complete cycle

$$\oint pdq = \int_0^{2\pi r} mvdx = 2\pi mvr = nh \qquad (1)$$

The derivation follows this condition much the same as in conventional derivations. The velocity term is eliminated from the equality of centrifugal and centripetal forces, or

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

which, on substitution in (1), yields

$$4\pi^2 rmZe^2 = n^2h^2 \qquad (2)$$

The total energy of the hydrogen atom is the sum of the kinetic and potential energies

$$E = {}^1/_2\, mv^2 + \int_\infty^r \frac{Ze^2}{r^2} = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \qquad (3)$$

With the elimination of r between (2) and (3), we have the conventional expression for the energy of the hydrogen atom, namely that

$$E_n = -\frac{2\pi^2 mZ^2e^4}{M^2h^2}$$

This derivation is as exact as one involving angular momenta and it has proved to be much more readily understood by the average student.

Chemical Semantics

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REPEATEDLY we have been told that it is the duty of an instructor to insist on accurate terminology. Occasionally, letters and articles in this JOURNAL indicate the interest of its readers in maintaining or establishing correct definitions and exact phrasing. In the face of this interest it would seem heresy to claim that adherence to "correct" terminology can sometimes do more harm than good.

THE BENZOYL DISPUTE

Toward the end of the eighteenth century Lavoisier, in classifying the elements and compounds, found it necessary to include an intermediate type that seemed to be both element and compound. He called it the "radical" and defined it as a group of elements that acts as a single unit and, like a metal, unites with oxygen. He believed that a radical was analogous to a metal and that union with oxygen was analogously its most important chemical property. In effect, the word "radical" had here two meanings, one based on the group permanence and the other on the affinity for oxygen. So long as the only known "radicals" fulfilled both meanings no one took the trouble to observe the double definition, and the two meanings were unconsciously regarded as synonymous.

In the early 1830's, however, the benzoyl and acetyl groups were studied. Liebig, Wöhler, and Dumas classed the benzoyl group as a radical because of its persistence throughout a series of compounds. Berzelius thundered against this view with what he considered irrefutable and rigorous logic. Benzoyl, he insisted, could not be a radical because it contains oxygen and a radical by definition is something that itself unites with oxygen: "A radical cannot be an oxide. The very meaning of the word radical indicates that it represents a body which is in union with oxygen" (*1*).

POLYMERIZATION

Polymerization was once (and still is, in most textbooks) defined as an increase in molecular weight without a change in elementary composition. It was therefore generally applied in organic chemistry to the *self-addition* of unsaturated compounds. In time it has come to be applied, especially in industry, to any reaction producing a considerable increase in molecular weight by the coupling of molecules, like or unlike, saturated or unsaturated. There is little resemblance in composition between benzyl chloride and its polymer, polybenzyl, produced by the Friedel-Crafts condensation:

$$n\mathrm{C_6H_5CH_2Cl} \rightarrow \mathrm{C_{7n}H_{6n}} + n\mathrm{HCl}$$

Certainly, benzyl chloride is not an olefinic or acetylenic compound, nor does it react by self-saturation of a double bond. Nevertheless, states Carothers (*2*), one can find instances in the literature where the fact that a reaction is called a "polymerization" is cited as proof that some unsaturated compound must be an intermediate product in the reaction.

LYOPHILE AND LYOPHOBE

Hartman cites the following case in his well-written textbook on colloid chemistry (*3*). Noyes called the attention of physical chemists in 1905 to the distinction between those colloids that were "nonviscid, nongelatinizing and easily precipitated by salts," and those that were "viscid, gelatinizing, and not easily precipitated by salts." He called the former "colloidal suspensions" and the latter "colloidal solutions." Because the "colloidal suspensions" did not settle out as "true suspensions" do and because the "colloidal solutions" could be separated into solute and solvent by dialysis unlike "true solutions," many physical chemists tended to reject the classification until Perrin and Freundlich introduced the Greek words that even the Greeks did not have for them, *lyophilic* and *lyophobic*.

ATOMS AND MOLECULES

In the eighteenth century the words "atom" and "molecule" were used interchangeably to mean a small particle. In 1808 Dalton suggested the relation between the combining weights of elements and the relative weights of the ultimate particles of elements and compounds. He referred to these ultimate particles as "atoms," whether of elements or of compounds. NaCl he would have called the "atom of salt."

Three years later Avogadro, impressed by Gay-Lussac's publication on the combining volumes of gases, drew from it one of the most fruitful conclusions in chemical history. Adopting Gay-Lussac's opinion that in the gaseous condition there is no appreciable attraction between the particles, he deduced with rigorous logic the uniform distribution of particles in all gases under the same conditions, the proportionality between gas densities and the relative weights of the particles, and lastly the complex structure of these particles. This last conclusion compelled him to split Dalton's "atom" into three terms: The *smallest possible* particle of an element he called the "elementary molecule"; today we call it the atom. The *independent* particle of a *gaseous element* he called the "constituent molecule," and the *independent* particle of a *gaseous compound* he called the "integral molecule"; today we call both of these simply the molecule.

But Avogadro's contemporaries were reluctant to follow him. In addition to experimental facts running contrary to the apparent consequences of his theory, there were objections seemingly based on logic but actually on logomachy.

The word "atom" seemed so much more precise than

"molecule" that chemists continued to use it in preference to the latter. What Avogadro called the "constituent molecule" of hydrogen they called the "atom" of hydrogen. But Avogadro concluded from Gay-Lussac's experimental data that this same "constituent molecule" was composed of two "elementary molecules," *i. e.*, atoms. Avogadro's contemporaries naturally expressed this by saying that

"his elementary molecule is half of an atom. But how can one have a half-atom if by very definition the atom[1] is indivisible? This is indeed absurd!"

Fidelity to terminological exactitude is no doubt one of the finer gifts of the classical education prevalent among scientific men in the early years of the nineteenth century, but even Dalton, who was only an indifferent scholar of Latin and Greek, had bound himself to his definition:

"I have chosen the word *atom* to signify these ultimate particles, in preference to particle, molecule, or any other diminutive term, because I conceive it is much more expressive; it includes in itself the notion of *indivisible*, which the other terms do not" (*4*).

On one occasion Dalton argued with a colleague in favor of his formulas for water and hydrogen peroxide, HO and HO_2,[2] respectively. The other formulas would require fractional ratios of atoms. This, the gentle Quaker triumphantly concluded, proved his own formulas to be correct, "for thou knows it must be so for no man can split an atom" (*5*).

The practice of using the term "atom" for the smallest particles of both elements and compounds led to another error. Associated with the idea of indivisibility, the term led chemists to assign unconsciously to the compound some of the stability characteristic of the element. Hence, it was difficult for them to imagine a reversible partial breakdown of compounds. Not until almost a half-century after Avogadro's publication were the anomalous vapor densities and molecular weights of ammonium chloride and sulfuric acid shown to be due to dissociation of these molecules in the vapor state, removing the greatest objection to Avogadro's hypothesis.

One of Avogadro's few converts was Dumas. Around 1826 Dumas adopted the hypothesis and expressed it ten years later in the form: "Equal volumes, equal numbers of atoms" (*i. e.*, equal volumes of gas, equal numbers of molecules). When it was objected that if this were true, the "atoms" are divided into two when gaseous elements react and that this is absurd, since atoms are indivisible, Dumas airily replied,

"Chemistry cuts the atoms that physics can't cut. That's all!" (*6*).

Dumas' contemporaries had none of his flippant attitude. They, indeed, tended to take the word "atom" too seriously. It was perhaps to avoid this tendency that Avogadro sedulously shunned the word. Instead, he wrote of half-molecules and quarter-molecules (*7*), which his contemporaries naturally translated literally as half-atoms and quarter-atoms. Moreover, he took the unit of molecular weight to be the weight of a molecule of hydrogen. This made the atomic weight of hydrogen fall on 0.5 and introduced many other fractional or mixed numbers to the table of atomic weights. Inevitably this supported the objection that Avogadro was dividing the indivisible. Ladenburg describes Berzelius as feeling that

"it is absurd to assume fractions of atoms, and says that it was formerly the custom to abandon hypotheses as soon as they led to absurdity" (*8*).

[1] Greek, *a-tomos*, not cut.

[2] Or equivalent, since Dalton did not use these letter symbols.

PHRASING AND MEANING

Admittedly, there is some value to efforts at improving word usage among our students or ourselves, but too often our efforts are wasted on trifles. A case in triviality is that of the physician who complained that "clinic" is used to mean bed-less institutions such as dispensaries and out-patient departments, whereas the Greek word *kline* meant "bed" (*9*). It is immaterial whether a titration be called a "volumetric" or a "titrimetric" procedure, since the meaning of the former is clear to any graduate chemist; its replacement by the latter word may, however, be justified in a classification of analytical procedures, to prevent confusion of titrations with gas-analytical methods (*10*). It is inexact meaning, not inexact phrasing, that confuses. This all the more so because the meaning is often tacit and implied.

Where a word has two or more meanings, the confusion may be both serious and unconscious. In the benzoyl controversy "radical" had come to have two different meanings, but Dumas and Berzelius seemed unaware of this. In the dispute over Avogadro's formulas, "atom" had at least three meanings: the chemical unit of the element, the physical unit of the element, and the physical unit of the compound. Only Dumas and Avogadro seemed to have noticed this, and the former not at all too clearly.

Another example of identification of dissimilar objects by using a single word for them is given by the reception of Faraday's law of electro-equivalence. A century ago the word "electricity" contained both the concepts of quantity (measured today in coulombs) and that of intensity (measured today in volts). Faraday himself pointed out that his law related combining weights only to the quantity of electricity and that it was the intensity of the current that was a measure of the chemical affinity. Nevertheless, Berzelius and other chemists between 1834 and the 1880's persisted in confusing the two aspects of electrical energy, thereby delaying acceptance of Faraday's law and the development of a consistent electrochemical theory of valence.

Another example is the confusion of temperature and heat in Newton's mind, a confusion due to his using for them the same word, "heat" (*11*).

Then, too, there was the derisive questioning of Arrhenius in the early days of the ionization theory,

"If sodium chloride dissociates in solution, why does not the sodium react with the water?"

Here "sodium" meant both the free metal, with its own characteristic properties, and also the common fundamental constituent of the compounds and allotropic forms of the element. This double meaning of "element" is a very common error, as we all know (*12*).

In none of these cases was the misunderstanding prevented by meticulous phrasing. In some, the error might have been prevented by careful definition of terms, but certainly not by holding to the traditional or etymologic definitions. There are reasons why apparently precise definitions, moreover, do not always prevent confusion of meaning.

DEFINITION AND MEANING

The bare formal definition of a chemical concept is often embellished or even obscured by subjective and sensual side-pictures. Geometrical figures and mechanical analogies are often necessary in teaching, especially in physics and physical chemistry, but they tend to leave a deeper impression than the formal logical definition. The human mind tends to prefer such side-pictures. A graduate student once told me that his mind pictured the electron as a "blue-hot ball of fire whizzing on a dotted curve around a bigger ball, the nucleus" .... Much might be done for chemical education by a well-trained psychoanalyst.

Moreover, definitions are themselves composed of words and often these latter are themselves in need of clear definition. Sometimes a definition merely transfers the ambiguity from one word to several. Sometimes the ambiguity is concealed by the apparently simple words composing the definition. In the definitions of element, compound, and mixture we frequently meet the undefined terms "pure," "simple," and "decomposed."

According to Bridgman (*13*), the meaning of a concept is merely the operation associated with either the concept or its measurement. Introducing a new technic or tool means introducing a new definition, or at least a new meaning. The introduction of X-ray diffraction changed the meaning of "crystalline" from "bounded by plane surfaces" to "possessing a definitely ordered internal arrangement of atoms and/or molecules." We can speak today of crystalline cellulose and of the crystal structure of stretched rubber. During the nineteenth century there were no methods available for separating elements into subspecies, so an element could then be defined as a non-decomposable simple substance. Since 1900 the positive ray beam, molecular rays, the mass spectrograph, and the separation of isotopes have caused us to split the element into its isotopes and to split accordingly the unit of atomic weight into the chemical unit (with $O = 16$) and the physical unit (with $O^{16} = 16$) We changed the definition of element, basing it on the atomic number as found by X-ray spectra. We changed "atomic weight" from "relative weight of an atom" to "mean relative weight of the atoms."

Frequently, if a definition is couched in abstract terms it remains unchanged in the textbooks after considerable change has occurred in the experimental technics. The teachers and students, writers and expounders, will then continue quoting the old definition, without realizing that the operational meaning is now something else.

CHANGES OF DEFINITION

Often "incorrect" usage is merely a change of definition, carried out unconsciously or tacitly. We may criticize those who are so undiscriminating as to fail to state explicitly the new definition, but we must admit that definitions can legitimately change.

Often a definition has been broadened so as to include a larger class, as: alcohol, alum, spinel, aldehyde, acid.[3] Or it may be restricted to a smaller class, for example: "isomerism" once included polymerism, but now it is restricted to cases where the molecular weights are the same. A definition may be changed in order to abandon a disproved theory or law. Berzelius (*14*) defined catalysis as "the decomposition of bodies by this [catalytic] force." Ostwald changed it to one based on reaction velocities. Or the definition may be changed so as to save a theory or law. Proust's argument with Berthollet over the definite composition of compounds was won partly by experimental proofs and partly by the decision to count only those substances as compounds that had a uniform definite composition. Thus a law was rewritten as a definition. This frequently happens.

Sometimes, however, we are free to decide which of two mutually dependent statements we shall call a definition and which we shall call a law. This is quite frequent in thermodynamics. Thus, we can define temperature as the linear function of the volume of the mercury in a mercury-in-glass thermometer and then show experimentally that the pressure–volume product pv of a gas is almost a linear function of this temperature (Boyle-Charles law), or we can define temperature in terms of the pv product of hydrogen at low pressures (perfect gas thermometer) and then show experimentally that mercury has an approximately constant coefficient of expansion. Again, the ideal gas has three equally valid definitions, any one of which can serve as *the* definition, the other two being then termed "laws" (*15*). In all such cases our choices of definition can be made to suit our convenience, and it is sheer pedantry to quibble as to which is definition and which is law.

[3] Originally *acetum*, vinegar.

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COPPER MIRRORS

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IT IS common knowledge that the reduction of cupric oxide with hydrogen is often attended by the formation of a copper mirror on the walls of the container. The writer's attention was directed to this problem by experiences of students in the elementary chemistry laboratory. These students were instructed to perform the familiar experiment of determining the equivalent weight of an unknown metal (copper) by reduction of the oxide. A diagram of the apparatus used is shown in Figure 1. This diagram is given because it offers a clue to the formation of the mirrors.

The apparatus consists of a generator in which hydrogen is prepared by the action of zinc on dilute sulfuric acid, a calcium chloride drying tube, and a pyrex test tube in which the actual reduction takes place. In the writer's experience a fairly large proportion of the students obtained copper mirrors on the inside of the pyrex test tube. These unfortunate students have, in the past, been instructed to repeat the experiment because of a mistaken belief that they had spilled copper oxide while introducing the porcelain boat into the test tube.

Formation of a mirror under the circumstances described implies the presence of a compound of copper which is volatile at a dull red heat or lower, and which is readily reduced by hydrogen. The oxides of copper are, of course, readily reducible, but they have no appreciable vapor pressure below 1000°C. The only volatile compound of copper appears to be cuprous chloride, which may be readily sublimed at a red heat. The statement sometimes appears in the literature that cupric chloride is reduced by hydrogen to cuprous chloride but that further reduction does not take place. It is true that for the reaction

$$2CuCl + H_2 \rightleftarrows Cu + 2HCl$$

the equilibrium lies very far to the left at room temperature. But at 400°C. the equilibrium constant approaches unity, and for still higher temperatures reduction takes place readily.

The first experiment tried in connection with this problem was to duplicate formation of the mirror. No mirror could be produced when tank hydrogen was used, but mirrors were often formed when hydrogen, prepared by the action of zinc and dilute sulfuric acid, was dried over calcium chloride. Formation of the mirror was attended by a green color of the burning excess hydrogen. This suggested that impurities in the hydrogen were responsible for the mirrors. The impurities to be expected are arsine, from arsenic in the zinc; sulfur dioxide, from reduction of the sulfuric acid; and hydrogen chloride, by action of sulfuric acid spray on the calcium chloride.

The next experiment was to introduce a drop of hydrochloric acid into the hydrogen stream used for reduction of the copper oxide. At once a mirror was formed. It seems therefore that the sequence of reactions leading to formation of the mirrors is:

$$2CuO + H_2 \rightarrow Cu_2O + H_2O$$
$$Cu_2O + 2HCl \rightarrow 2CuCl + H_2O$$
$$2CuCl + H_2 \rightleftarrows 2Cu + 2HCl$$

Conversion to the chloride may precede reduction of the divalent copper.

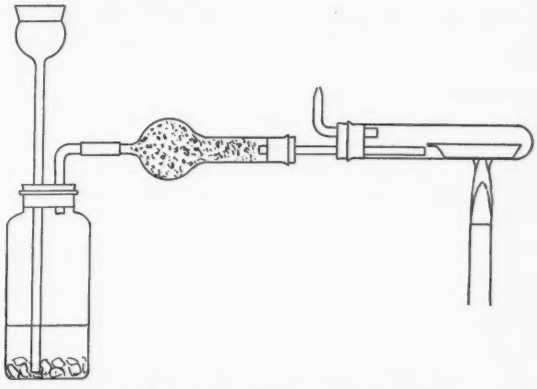

FIGURE 1.—APPARATUS FOR DETERMINING THE EQUIVALENT WEIGHT OF A METAL

Pure cuprous chloride was next substituted for cupric oxide. A good mirror was produced almost as soon as the cuprous chloride melted. By appropriate heating, the mirror could be produced at will either adjacent to the porcelain boat or several centimeters away. Sometimes the mirror was so thin that it was green by transmitted light. No reduction to metallic copper took place in a nitrogen atmosphere, proving that the reaction is actually reduction rather than decomposition.

An effort was made to see if an analytical method for copper could be devised. This would be analogous to the Marsh test for arsenic. The method proved, however, to be rather insensitive, although a green color is imparted to the flame of burning excess hydrogen by as little as 0.1 mg. of cuprous chloride.

This semester, for the first time, the students in the writer's classes were instructed to fill their calcium chloride tubes with a mixture of calcium chloride and quicklime. Not a single copper mirror was observed.

Thermodynamics for Undergraduates in Chemical Engineering[1]

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THIS paper is concerned with three educational phases of the subject: the purpose of the course as related to the curriculum as a whole; the objectives desired and the philosophy for developing such a course; and a description of one method employed in teaching it.

I. PURPOSE OF COURSE AS RELATED TO CURRICULUM

Why should undergraduates take a course in thermodynamics? This question can best be answered by first examining the subject matter relating to thermodynamics as treated in physical chemistry. After studying physical chemistry, our undergraduates usually have a workable understanding of the first law equation for the non-flow process, of thermochemistry, of the relation of standard free energy ($\Delta F°$) to equilibrium constants, and of the effect of temperature on $\Delta F°$ for low pressure reactions. A thorough understanding of these four topics is not too much to expect from two semesters of physical chemistry. In fact, in some instances this undergraduate study in physical chemistry is extended to include some of the advanced material in thermodynamics as presented by Lewis and Randall (*5*). In this connection, another point worth mentioning is that physical chemistry is usually taught by members of the chemistry department who have a purely scientific rather than an engineering viewpoint. This arrangement is, in my opinion, quite satisfactory and is even to be encouraged in that it gives the undergraduate a broader outlook.

The course in physical chemistry thus serves as an introduction to thermodynamics. It does not, however, include a broad enough foundation to suffice for chemical engineering applications. For example, it does not include the basic equations for the steady flow process or the application of the entropy function to engines, turbines, and compressors. Consequently, it is quite unlikely that even the best course in physical chemistry will supply the needs of our undergraduates in chemical engineering.

As a possible alternative, a course in mechanical engineering thermodynamics might well be considered. Unfortunately, this course seems to be governed by a different philosophy from that desired—a philosophy which allows the solution of problems without a complete understanding of the fundamentals. Moreover, formulas are used to such an extent that solving problems is usually a matter of finding the right one and "turning the crank" to arrive at an answer. Furthermore, the fluids studied are limited to air, water, and refrigerants. Hence, such a course could never fill the needs of a chemical engineering B.S. graduate, who frequently encounters problems involving the energy effects in a contact sulfuric acid plant or the power requirements for compressing a hydrocarbon gas mixture. The conclusion from this discussion is obvious: neither physical chemistry nor mechanical engineering thermodynamics can possibly meet the needs of our undergraduates in chemical engineering.

As for chemical engineering, there is the task of reviewing and extending those four topics studied in physical chemistry, of developing some new ones, and of applying the whole to practical problems *with an engineering viewpoint.* Certainly the logical course for accomplishing these objectives and for systematically studying energy transformations and equilibrium relations is chemical engineering thermodynamics.

Such a course in the present-day curriculum for undergraduates in chemical engineering should serve a fivefold purpose. First, it should extend the study of energy in physical chemistry from the batch or non-flow processes to the steady flow processes. Second, it should lay a firm foundation for developing both energy and equilibrium relationships as well as the properties of materials for application in other courses. Third, it should present a general background for a *unified* approach to: the use of physical and chemical data for flow processes, properties of materials, power generation, compression of gases, refrigeration, chemical equilibria, fluid flow (especially Bernoulli's equation), "heat balances" and their limitations, and for such unit operations as distillation and humidification. (In this respect it functions as a sound core from which the several portions may be withdrawn as needed and applied to related problems in other subjects. Hence it serves as a useful tool for handling problems in chemical technology, unit operations, and plant design.) Fourth, it should include an application of its own basic relationships to evaluating the properties of fluids. Lastly, it should include the solution to problems in chemical engineering which cannot otherwise be solved.

II. OBJECTIVES AND PHILOSOPHY OF COURSE

Before a suitable course can be developed, it is first necessary to decide upon its objectives and to formulate a philosophy for teaching.

[1] Presented before the Society for Promotion of Engineering Education, Ann Arbor, Michigan, June 24, 1941.

The objectives of teaching thermodynamics to chemical engineering undergraduates may be enumerated as follows:

1. To develop an understanding and an appreciation of the utility of energy and equilibrium relationships, as separate and distinct from material balances.
2. To drill and discipline the student in straight thinking about energy, equilibrium, and physical and thermodynamic properties of materials.
3. To develop the ability to resolve seemingly complex problems into simpler ones, and then to determine what data, values, or conditions are needed to solve the several simpler portions. In developing the analytical ability of the student, thermodynamics is supreme.

When the student begins his study of thermodynamics, he is either taking simultaneously or has just completed an intensive course in material balances, generally known as stoichiometry. His next step on the educational ladder in chemical engineering is a study of energy transformations, followed by that of equilibrium relations. Thus all problems dealing with rate of reaction are ruled out until the undergraduate takes up unit operations, applied kinetics, or plant design. This point is specifically mentioned in order to place an upper limit on the scope of a thermodynamics course, especially since some writers include subject matter dealing with rate of reaction and thus make thermodynamics rather all inclusive.

Because of the abstract thinking involved, thermodynamics is usually a difficult subject for the beginner to grasp. This difficulty is partly alleviated by purposely creating an early interest through practical application. Consider a simple heat exchanger with steam initially superheated, flowing countercurrently to propane gas under pressure and with large pressure drops for both streams. The problem is to find out how much propane can be heated per hour with a given amount of steam per hour. The solution of a gas-to-gas low pressure exchanger is relatively simple. However, the undergraduate, when asked to solve this propane-steam problem without a knowledge of thermodynamics, would most likely obtain an answer by employing the so-called "heat balance," totally unaware that such a balance would not apply where propane gas enters at a high pressure and where, further, the temperature difference must be finite and in the proper direction required by the second law. Several typical problems like this are presented to the class early in their study to bring out the important and necessary attitude that thermodynamics is practical. Some other examples which serve the same purpose are: solving refrigeration problems with a Mollier diagram; computing the conversion of sulfur dioxide to trioxide in an adiabatic catalyst chamber; calculating the true efficiency of a rectification column; economically distributing the power and process steam loads in a process industry by using extraction turbines, accumulators, and evaporators; and finding the temperatures, total pressures, and maximum conversions in a high pressure synthetic process, *e. g.*, ethanol by hydrating ethylene.

The instructor concerned with the students' interest in such a course may well ask himself: *Is it possible to develop in the student an enthusiastic attitude founded upon the usefulness of thermodynamics to engineering problems?* Or is this a course which appeals to the better mentalities and consequently leaves the average student in deep water? Can the interest of the student be maintained throughout the course, as is usually true in unit operations? There is, of course, no definite answer to these questions. But in my opinion interest may be created and maintained by continually citing practical applications thoughout the course. Usually the early part of this course is necessarily abstract, and it requires both time and patience to develop clear-cut pictures of the concepts involved. After this elementary period the student begins to grasp the idea that thermodynamics serves as a means for a *unified* approach to many problems in chemical engineering. Accordingly, his interest develops, and, as the practical applications are brought out, some students even become enthusiastic over the subject. My experience has shown, however, that active interest can be developed only through emphasis on thoroughness, not on covering ground. If the student appreciates the usefulness of thermodynamics by the time he graduates, the instructor might well be satisfied.

III. METHOD OF TEACHING

There are no doubt several effective methods of teaching chemical engineering thermodynamics to undergraduates. After trying several arrangements, the writer has adopted the technic which is described below. This description is offered with the thought that it may prove helpful to those beginning the teaching of such a course.

The text used in the course is Weber's "Thermodynamics for Chemical Engineers" (*7*), supplemented by Hougen and Watson's "Industrial Chemical Calculations" (*2*), and by Kiefer and Stuart's "Principles of Engineering Thermodynamics" (*4*), and illustrated by lantern slides. As a general rule, a definite number of pages in the text is assigned to supply the basic information on a given topic. The lectures are for the most part informal, with opportunities for questions asked by the class. The lecture period may be used in several ways: to quiz the class orally on the reading assignment, to emphasize by discussion the significant points, to supplement the text material either by further discussion or by solving an illustrative problem, to explain the details of derivations, or to illustrate industrial equipment by means of lantern slides. Despite all efforts to get the information across to students, this procedure is apparently not effective without requiring them to apply the principles by solving problems that provoke thought.

In order to emphasize the necessity for solving these

problems the class is given a set each week. To permit a discussion of the fine points, the class meets in smaller sections, usually not exceeding twenty students. For the sake of variety, these sections are conducted in three different ways, depending upon both the length and complexity of the problems. In the first, the student goes to the blackboard, puts on his solution, and is questioned by both instructor and students either as to method or details. Frequently, one student will be asked to explain only a portion of the problem, leaving the remainder to other members of the section. This method is perhaps the most effective of the three, although it has the disadvantage of taking considerable class time, with the consequent danger of lagging interest. In the second method, the instructor quizzes different students on the solution and writes on the blackboard the several steps in the solution as given by the class. In the third method, a portion of the class is sent to the blackboard and each member writes out part or all of his solution. Each is allowed to explain his own solution to the class and usually is questioned as to the hows and whys. These three methods of handling the problem sections lend variety and allow flexibility in carrying out this part of the instruction.

Each major topic of the course is followed by an hour quiz. These are usually "open-book" and consist of problems that require more thinking than do the usual routine problems. To cite one example of the type of quiz given, after the class has studied "Heat of Reaction" and solved the related home problems, the quiz may be on the energy effect of an electrolysis, thus requiring a further interpretation of the terms in the steady flow equation.

The subject matter included in such a course is modified in both arrangement and content from that in the text. Briefly it is somewhat as follows:

1. *Fundamental Concepts and Definitions.* Assigned, then discussed in class with reference to experiment and including several illustrative examples. Typical problems to arouse the interest of the class are included here.

2. *First Law.* Carefully discussed regarding experimental basis. Units and their conversion. A Mollier diagram for carbon dioxide is passed out to the class for solving simple problems to bring out the differences among Q, W, ΔE, and ΔH. Problems are assigned. During the period of solving first law problems, much of the descriptive material in the text relating to physical chemistry is assigned and discussed. This material includes: equilibrium, the phase rule, phase relations of one-component systems, properties of materials, including approximations and properties of "wet mixtures." For this last item, the Keenan and Keyes (*3*) steam table is explained and used in solving problems where water is the fluid.

3. *Heat Capacity.* Assigned, discussed, and one set of problems illustrating use of both charts and equations.

4. *Heat of Reaction.* Emphasis on use of ΔE and ΔH. Illustrative problems solved in class and by outside assignment, followed by a quiz requiring further thought on the application of the first law equation as previously mentioned.

5. *Perfect Gases.* Detailed discussion of derivations for energy effects of isothermal, adiabatic, and polytropic changes of state.

6. *Gas Compressors.* Descriptive terms and the derivation of equations for power and volumetric efficiency. Mechanical details, construction, and industrial installations illustrated by lantern slides.

7. *Second Law.* Lecture on the second law and derivations following, primarily for the purpose of getting all this information before the class for a detailed discussion of the logic involved. Illustrative problems on entropy calculations. Home problems on heat engines and entropy calculations.

8. *Interpretation of Second Law Principle.* Detailed discussion of free energy, availability, and irreversible processes, especially Bernoulli's equation. Illustrative and home problems.

9. *Power Cycles.* Description and derivation of energy relations for Rankine cycle, supplemented by discussion of material in Kiefer and Stuart (*4*). Steam power plant equipment illustrated by lantern slides.

10. *Steam Engines and Turbines.* Descriptions, derivations, and lantern slide illustrations showing mechanical details, construction, and installations. Material in Kiefer and Stuart (*4*) is quite helpful. Problems on engines and turbines and especially on the distribution of power and process steam.

11. *Fluid Flow.* Supplementary to usual fluid flow as presented in unit operations, including the significance of $\int V dP$, flow through nozzles and orifices with large pressure drop, and natural gas transmission lines.

12. *Refrigeration.* Description, use of Mollier diagrams for solving problems, and lantern slides of equipment. Enthalpy–concentration chart for ammonia absorption machine.

13. *Generalized P–V–T Relations.* Compressibility factor for P–V–T relations in terms of reduced quantities (and generalized correlations for fugacity and isothermal enthalpy and entropy changes). May be earlier in course.

14. *Utility of Standard Free Energy.* Use of $\Delta F°$ for calculating equilibrium conversions, for deciding feasibility of a chemical reaction, and for computing true thermodynamic efficiency.

15. *Industrial Chemical Applications.* Comprehensive problems on industrial processes, such as ammonia oxidation for nitric acid. Problems on utility of enthalpy–concentration chart in evaporation, distillation, and crystallization. These types of problems perhaps have the greatest educational value in that they require the student to apply thermodynamics through his own thinking.

It is not unusual to find that the final semester draws to a close before as much subject matter as outlined above can be studied. Should this be the case, it is strongly recommended that the subject matter be reduced rather than sacrifice thoroughness. In timing the course, experience indicates that it is better to maintain the interest of the student by spending time on practical engineering problems rather than on theory or on pure logic.

It seems appropriate to mention the timing and coördination of chemical engineering thermodynamics with related courses. Both timing and coördination are important in effectively presenting thermodynamics. One example in timing those related courses is shown by the following tabulation:

Course	Semester			
	Junior Year		Senior Year	
	I	II	I	II
Physical Chemistry	x	x	..	..
Chemical Technology	x	x	..	..
Chemical Engineering Thermodynamics	..	x	x	..
Unit Operations	..	..	x	x

From the above tabulation, it is seen that the first semester course in thermodynamics is preceded by a semester of physical chemistry, that it is taken simul-

taneously with the second semester of physical chemistry and of chemical technology (inorganic and organic processes), and that the second semester course is taken with the first semester of unit operations. This arrangement has certain advantages in allowing the subject matter to "soak in" first through physical chemistry as an introduction, then through the first semester of thermodynamics itself, and finally through applications of the second semester course. Furthermore, this arrangement has the advantage of permitting *coördination* in thermodynamics with chemical technology and unit operations by means of such topics as: heat effects and equilibrium relations in both sulfuric acid and hydrochloric acid production; percentage conversion through $\Delta F°$; utility and limitations on heat recovery apparatus; interpretation of Bernoulli's equation and its application for large pressure drops. This coördination tends to restrain the emphasis upon individual courses and thereby create the impression upon the undergraduate that an education is not passing a certain number of courses, but learning how to understand, coördinate, and correlate the subject matter of these courses.

Unfortunately, not all our undergraduates realize the importance of correlating the subject matter of their several courses. As far as thermodynamics is concerned, with the above described arrangement seniors may elect —and a few do—a graduate course in chemical engineering thermodynamics given during the second semester. In general, this graduate course does not duplicate the subject matter of the undergraduate course but rather includes more advanced topics such as the effect of P, V, and T on properties, high pressure reactions, partial molal quantities, vapor–liquid equilibria, and enthalpy–concentration charts (construction and consistency), all with reference to practical problems.

In conclusion, it seems appropriate to express the thought that any effective method of teaching thermodynamics can be realized only after several have been tried. Even then the method adopted must necessarily be modified from year to year to suit the class.

ACKNOWLEDGMENT

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History of Chemistry in America

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A COMPLETE history of chemistry in America, which shall give a full account of chemical origin and developments in the various fields of exploration, agriculture, industry, education, research, economics, and national welfare, has not yet been written, although the need of preparing such a history has long been recognized.

The first attempt to prepare a history of chemistry in America was made by Benjamin Silliman, Jr., in 1874, in a report which he read as a part of a program of the general meeting of American Chemists, held at Joseph Priestley's old home in Northumberland, Pennsylvania, on August 1, 1874, to commemorate the one-hundredth anniversary of Priestley's discovery of oxygen. Silliman's report entitled "American Contributions to Chemistry" consisted of a short account of origins and early developments in the eighteenth century, and of brief reviews of the life and work of some 160 American chemists during the first three-quarters of the nineteenth century. It was published in the issues of *The American Chemist* for August–September, 1874, December, 1874 and March, 1875. These serial articles were afterward assembled and printed in book form. The first half of Silliman's essay dealing with the work of deceased chemists is elaborated more fully than the second half which consists largely of an itemized list of the publications of the American chemists living at the time the review was written. The treatment is therefore necessarily uneven and the work makes no pretensions of being a finished history of American chemistry. It will always be, however, a valuable starting point for the student of chemistry in America down to the time of the Priestley Centennial, and for this period it is about our only source of information concerning many lesser known chemists. Silliman's publication was much consulted by subsequent writers, some of whom have been grossly careless, or negligent, in their failure to indicate the source of their information and citations.

[1] U. S. Bureau of Agricultural Chemistry and Engineering.
[2] Curator, Edgar F. Smith Collection in the History of Chemistry.

Following the pioneer work of Benjamin Silliman, Jr., came Henry Carrington Bolton, who will long rank as America's leading bibliographer of chemistry. His bibliographies of chemistry books, chemical dissertations, and chemical journals should be found in the library of every student of the history of chemistry. They give one a convenient means of estimating the development of chemistry in America during the nineteenth century. One notices, for example, that the number of chemical books listed by Bolton as published by native authors in the United States for the decade of 1830 was 17; for the decade of 1840 it was twice this figure, or 33; and for the decade of 1850 it was over three times this figure, or 54. During the critical Civil War decade of 1860 the number sank to 38; during the reconstruction decade of 1870 it rose to 57; and then in the wonderful decade of 1880, when the modern period began, this number was about tripled when it rose to 163. The chief centers of chemical publication during the nineteenth century were New York, Philadelphia, and Boston. In the period up to 1860, Bolton lists 35 books as published in New York, 34 in Philadelphia, and 9 in Boston; in the period from 1860 to 1890 the numbers were 76 for New York, 43 for Philadelphia, and 11 for Boston. It was chiefly in the decade of 1880 that the phenomenal rise of New York as a center of chemical book publication occurred. A whole paper could be devoted to the interesting historical correlations which one can draw from a study of Bolton's bibliographies, but we must leave these for the time when the history of chemistry in America is to be written as a whole.

We come next to the mention of the historical and biographical works of the founder and most influential figure in the history of chemistry movement in America —Edgar Fahs Smith. Time is lacking to enumerate even the titles of Dr. Smith's works in this field. In a conversation with me upon the subject some years before his death, he disclaimed the title of historian. In his numerous biographical sketches, some 20 in number, his aim was humanistic rather than historical. He objected strongly to cluttering up his pages with bibliographic references which as we know are one of the supposed identification marks of the historian. Dr. Smith was the greatest humanitarian in the ranks of American chemistry. The development of theories, the founding of chemical industries, and the fixing of dates did not interest him so much as the personalities of chemistry. He was a master of the living phrase and no one could equal him in the ability to present, before students and the members of our meetings, vivid breathing likenesses of the great men who had promoted the growth of our science.

Above all things Dr. Smith was anxious, in connection with the establishment of this division, to found a journal that would be devoted to the publication of researches in the history of all phases of American chemistry from the time of the first settlements down to the present and, when the field had been sufficiently explored, that would serve as a basis for writing a comprehensive history of chemistry in America. The question now before us at this 21st anniversary meeting, when our division may be said to have come of full age, is whether the time is now ripe for an execution of this plan and if so what steps should we take to carry it into effect.

Preliminary to a discussion of this question it might be well for us to take an inventory of some of the sources of information concerning the early history of chemistry in America. Of the various sources of such information I would mention:

1. The unpublished documents and the published proceedings and contributions of the various historical societies. Of outstanding importance in this class are the valuable Winthrop papers in the library of the Massachusetts Historical Society in Boston which throw a flood of light on early chemical activities during the seventeenth century in colonial New England. Not all of these papers have been published, and their study offers a most attractive field for original historical chemical research.

European academies of science had correspondents in many of the American colonies and the colonial archives of these academies have many manuscripts of chemical interest. I would mention as an example the original letters of John Clayton on the chemical resources of Virginia, written in the 1680's to the Royal Society and now preserved in its library. Even where such documents have been published, a comparison with the original papers often discloses omissions, from one cause or another, of materials of great chemical interest. Members of our division are urged to explore the records of their state or local historical societies. Much interesting chemical information is often found buried in the pages of town histories and county gazetteers.

2. A second source of information about early chemistry in America are the printed accounts of travelers from European countries in the eighteenth and early nineteenth centuries. Buried away in these volumes many scattered references can be found to the chemical interests and activities of the American people in various parts of the country. The comments, both favorable and unfavorable, are highly instructive, as they illustrate opinions of foreign observers with different points of view. Among important publications of this class may be mentioned—The Swedish botanist Pehr Kalm's "Travels into North America" in the years 1748–51; the German physician Dr. Johann Schoepf's "Travels Through Some of the Middle and Southern States of the North American Federation in 1783–1784"; and the English observer John Melish's "Travels in the United States of America in the Years 1806 and 1807 and 1809, 1810 and 1811." Dr. Jane Louise Mesick in her "The English Traveller in America, 1785–1835" enumerates 77 different authors, whose works may be consulted with profit.

3. A third very informative source of information on chemical activities in America in colonial and later times are the industrial, economic, and commercial histories of America. In this class we will mention only Dr. J. Leander Bishop's very excellent "History of American Manufactures from 1608 to 1860," published in two volumes in 1861 and 1864. This scholarly work gives one of the best historical accounts of early American chemical industries that has yet been written. A specially valuable feature of Bishop's history are very complete footnote references to original sources of information. The student who will read Bishop and look up his citations will not only have obtained a fundamental knowledge of the origins of the salt, glass, potash, powder, tinning, distilling, dyeing, metallurgical, paper making, and other chemical industries of America but in acquiring this knowledge he will have received so thorough a practice in historical chemical research that he may be trusted to make independent researches in this field for himself. In 1867 several collaborators published a third volume of Bishop's history which gives a special history of individual manufacturing establishments in the United States that were operating at that time.

4. A fourth source of information about material for the history of chemistry in America includes published biographies, obituary sketches, diaries, letters, and other personalia of American chemists. These include such books as Water's "Sketch of the Life of John Winthrop the Younger," Fisher's "Life of Benjamin Silliman" in two volumes, Edgar Smith's "Life of Robert Hare," Elizabeth Osborne's "From the Letter-files of S. W. Johnson," the life of "Charles Anthony Goessmann" by the Corporation and Associate Alumni of the Massachusetts State College, and the life of "Ira Remsen" by our late lamented fellow member, Dr. Frederick Getman, who at the time of his recent death was working on the biography of another eminent American chemist, "John Mallet." To this class belong also autobiographies such as that of the late Harvey W. Wiley. Sketches of American chemists in our dictionaries of biography also supply much valuable information. These are all the more useful when references to source material are given. The "Cyclopedia of American Biography" contains 120 names classified under Chemists, to which must be added 13 other names classified under Agricultural Chemists and four other names classified under Biochemists. These classifications, however, are not satisfying, for the names of many whom we consider to have been prominent chemists are classified under other designations. Thus Benjamin Silliman, Sr., is classified under Professors, Thomas Sterry Hunt under Geologists, and Joseph Priestley, Samuel Mitchill, Chester Dewey, Amos Eaton, Parker Cleveland, and Persifor Frazer under Scientists. Much more satisfactory is White's "Compendium of American Biography" which gives a list of 381 American chemists whose sketches are given in the "National Cyclopedia of American Biography." Some chemists of importance have been overlooked by the editors of these cyclopedias and our division might do a good work in helping to correct such oversights.

The Proceedings of our National and State Academies of Science and of our various scientific societies can also be consulted to advantage. The example of Dr. Smith, who excelled in the field of biography and helped rescue many lives of American chemists from oblivion, should continue to inspire the members of our division, which since its establishment has presented on its programs biographical sketches of many American chemists. Personal letters and other private manuscript material constitute a very valuable source of biographic information which should not be neglected in research work of this kind.

5. Teachers in our colleges and universities have been the leading guiding spirits in the history of American chemistry. Our professors of chemistry for a period of nearly two hundred years have generally been versatile men who participated not only in educational affairs but exerted a profound influence on the industrial, civic, military, and economic welfare of the nation. To be convinced of the truth of this statement one has only to read the papers of the symposium on "Chemical Education in America" in the Edgar Fahs Smith memorial number of the JOURNAL OF CHEMICAL EDUCATION for April, 1932. We might almost say after reading these papers: "The history of chemical education in America is the history of American chemistry itself."

The historic records of chemical education in America, as preserved in the archives of our colleges and universities, constitute a fifth and most important source of information for many phases of American chemistry. These records may consist of outlines of curricula, manuscripts of lectures, student note books and theses, personal letters, museum collections (such as old apparatus, chemical exhibits, etc.), and other memorabilia. Members of our division connected with the older universities could render a valuable service in this connection. I would call especial attention to the valuable historic chemical documents in the library of Yale University. Here are the original manuscript diaries of President Ezra Stiles which throw much light on chemical matters in the second half of the eighteenth century not only at Yale and other colleges but in the country at large. Here also are the immense manuscript collections of the elder Silliman, consisting of nine volumes of autobiographic reminiscences and 17 volumes of journals which are invaluable to the student of American chemistry from 1800 to 1860. Some of this material was made use of by Fisher in his two-volume life of Silliman, but there is much there of chemical interest that Fisher passed over which should be edited and published.

6. In addition to the five classes of source material upon the history of American chemistry previously noted, there is a sixth miscellaneous class of statistical and economic importance, such as Census Reports, Patent Reports, and various industrial economic surveys. As examples of this class of source material may be mentioned the chemical report of Friends of Domestic Industry (Oct. 26, 1831) which gives the first statistical survey of American Chemical Industries, and the exhaustive report of Munroe and Chatard on the Chemical Industries of the United States for the Twelfth Census—a report invaluable for its wealth of historical and statistical information.

It is the opinion of the committee that before a comprehensive history of chemistry in America can be written it is necessary to prepare as complete a card index as possible of all material, published and unpublished, that is available upon the subject. Such an index should include not only all the items in the previously mentioned classes of source material, but all the published and unpublished contributions on the history of chemistry in America by members of the American Chemical Society, especially of those who belong to or have belonged to our Division of the History of Chemistry. A compilation of the titles of 150 papers on this subject that have been published in the JOURNAL OF CHEMICAL EDUCATION has been made. These should be transcribed to index cards, when the form of the latter has been agreed upon, with name of author, time and place of publication, title of paper, and a brief statement regarding the nature of the historic material contained therein.

Historic material on American chemists and chemistry published in other journals should be indexed in a similar way. These will include biographical sketches (such as those published in the American Contemporary Series of the *News Edition*), obituary notices, and the immense range of miscellaneous historic material published in the *American Journal of Science*, the *American Chemist*, the *Journals of the American Chemical Society*, *Science*, the *Science Monthly*, etc., and the many trade journals devoted to special industries. When the work of indexing has well advanced, classification of the cards can be commenced under the various designations, such as Chemistry among the American Aborigines; Chemistry among the early Spanish, French, and English Explorers; Alchemy in America; Chemistry in each of the American Colonies, etc., etc. When the indexing has reached a satisfactory state of completeness the classified references can then be typed for mimeographing or publishing as a bibliography for the benefiit of a publication committee when it is desired to undertake the actual writing of the proposed history. It will take the combined efforts of members of our division over a period of several years to make an indexed survey of the history of chemistry in America along this line, but it is a work which deserves undertaking.

The most convenient clearing center and repository for card index files on the history of chemistry in America is the Edgar Fahs Smith Memorial Collection of the University of Pennsylvania in Philadelphia. Miss Eva V. Armstrong, the curator of this collection, has consented to this arrangement and has offered to arrange for the revision of the lists submitted by the collaborators, for the typing of the cards, for their filing alphabetically by authors, and for their possible later classification under a few subject headings. The card files thus prepared would be kept as a permanent part of the Smith Memorial Collection in the History of Chemistry and would be kept up to date by making a semi-annual survey of papers appearing on American Chemistry. Copies of reprints of papers on the History of Chemistry in America might also be deposited in the Smith Collection.

Manuscripts of papers on the History of Chemistry in America that have been read before our division but not published should be obtained so far as possible from their authors and copies deposited in the Smith Memorial Collection for inclusion in the proposed survey. An inspection of the past programs of our History Division will enable us to determine the titles of such papers and perhaps to trace their location.

Progress in the Preparation and Determination of the Properties of Boron[1]

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BORON is the only common element, solid under ordinary conditions, whose crystal structure is not known and whose properties are not well understood. This is surprising when one considers that compounds of boron have been easily available and have been exploited for a very long time. The use of borax as a metallurgical flux goes back to antiquity, and boric acid was isolated from borax by Homberg in 1702. In 1807 Davy (*1*) reported the electrolytic decomposition of boric acid, and in the following year Gay-Lussac and Thenard (*2*) obtained boron as a black powder by the reduction of boric acid by potassium. They identified their product as a new element, to be placed beside carbon. Davy (*3*) independently studied the same reaction and confirmed the findings of Gay-Lussac and Thenard.

Since that time a large number of investigators have worked on the preparation of boron. A critical survey of their work leads to the conclusion that in many cases the samples obtained undoubtedly were very impure. The samples have been shown to possess many interesting properties, but the reports are conflicting in many respects, probably due to the variation in kinds and amounts of impurities. Unfortunately, the few investigators who have prepared what probably were the purest samples have not investigated their properties extensively. In no case have single crystals been described.

Boron possesses certain features of atomic structure which make this element of exceptional interest. The very small atomic size and the large charge of its simple ion should give it a tendency for covalent non-metallic behavior. On the other hand, it has only three valence electrons and therefore boron atoms, by bonding together, cannot achieve a stable diamond-like tetrahedral covalent structure, with each atom attaining an octet of electrons, but might rather be expected to act as a metal. The unique combination of very small size and three valence electrons makes it impossible to predict the properties to be expected, but lead one to suspect hybrid character. The coördination and bonding in the crystalline element probably are unusual.

The scanty information now available about the structure of the borides gives some indication of what boron–boron bonding may be like. In FeB each boron atom has two boron neighbors close to it at 1.77 A.; in AlB_2 each boron atom is surrounded by three others at 1.73 A. in graphite-like sheets; in the hexaborides, such as CaB_6, there is a three-dimensional network of boron atoms with each boron having five nearest neighbors at 1.72 A. In all cases extensive boron–boron bonding is evident. The properties of such borides lead one to suspect that the bonding may be essentially that characteristic of intermetallic compounds. The metallic bond may well be the best answer for the bonding in crystalline boron. It is likely, therefore, that the massive element may possess a unique combination of properties. The reports of great hardness, highly refractory nature, metallic luster, and interesting electrical properties indicate that this is true.

The dearth of exact information about boron is due to the considerable difficulties encountered in attempts to prepare pure boron, especially in the massive single crystalline form. These difficulties arise from a variety of factors. At the elevated temperatures required for the reduction of its compounds, boron is very active toward other elements and forms compounds of high stability and inertness. These compounds are not easily separated from the element. Boron does not build up large crystals readily, but shows a considerable tendency to assume the vitreous condition. It is highly refractory, with a melting point reputed to be at about 2200°C., and the problem of fusing a powder sample to give the massive material, without getting reaction with the refractories in contact with it, is difficult of solution. The analytical methods for boron are not highly exact and it is not an easy task to establish the degree of purity of samples accurately. Spectroscopic analytical methods will not indicate impurities such as oxygen. X-ray diffraction patterns characteristic of this element are not established, and its atoms have such a low scattering power for X-rays that long exposures are necessary and even small amounts of impurities may give misleading patterns.

The preparation of pure boron and the determination of its properties have challenged the ingenuity and skill of the investigator and many have attempted to overcome the difficulties involved. The authors are continually being surprised to find one chemist after another who has devoted some attention to the problem. A great deal of work has been done which has never been reported in the literature. Industrial research laboratories have supported much research on boron and a great number of patents have been taken out. Gradually more elegant methods for obtaining boron have been devised and better technics have become available for studying the products. Slowly, as

[1] This article is based upon part of a paper presented at the Sixth Annual Symposium of the Division of Physical and Inorganic Chemistry of the A. C. S., Columbus, Ohio, December 31, 1941.

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new tools are tried, progress is being made, and it is to be hoped that in the near future adequate fundamental information may be supplied.

REVIEW OF METHODS WHICH HAVE BEEN USED TO PREPARE BORON

The problem of producing boron involves its extraction from suitable compounds. Fortunately, adequate supplies of starting materials are abundant. Borax, boric acid, and boric oxide are easily obtained in a high state of purity and have been widely used. The halides of boron are readily prepared and purified and, because of their volatility, may conveniently be exploited. The fluoborates and the hydrides also have been tried. These compounds have been subjected to the action of a large variety of reducing agents over a wide range of conditions. Electrolysis of the fused compounds has been tried, and attempts to get free boron by thermal decomposition have been made. A summary of these experimental methods and the results obtained will illustrate the difficulties encountered and the progress that has been made in overcoming them.

Reduction of Compounds of Boron by the Metals

The more active and common metals have been used extensively for the reduction of the compounds of boron at high temperatures. Sodium, potassium, magnesium, calcium, aluminum, zinc, and iron have been found to be effective. After reduction has been accomplished, substances other than boron are removed as thoroughly as possible by treatment with such reagents as water, hot hydrochloric acid, alkalies, and hydrofluoric acid. Boron is reputed to resist attack by such reagents but to react with hot concentrated nitric acid. In spite of such purifying treatment, the black powdered boron which is obtained has been found to be badly contaminated with inert borides of the metals as well as with the inert and stable boron nitride, and considerable percentages of oxygen may also be present.

The method most commonly employed to prepare boron involves the action of magnesium on boric oxide at high temperatures. The black powder obtained is referred to as "Moissan's Boron" because Moissan (*4*) worked out the conditions most favorable for its production. He used a large excess of boric oxide to prevent the formation of magnesium borides and boron nitride. After ignition, the product was treated with hot hydrochloric acid, water, 10 per cent alcoholic potassium hydroxide, water, and 50 per cent hydrofluoric acid, and the residual powder was dried over phosphorus pentoxide. Analysis of several samples gave average compositions of 95 per cent boron and 3 per cent magnesium. Fusion of this powder with boric oxide removed some of the magnesium but the boron content could be raised to only 98.3 per cent and 0.37 per cent of magnesium was still present. Moissan was convinced that a very inert magnesium boride, insoluble in hydrochloric acid and nitric acid, was present. Many other workers have studied the use of magnesium for producing boron and they have confirmed Moissan's conclusion that it is impossible to produce pure boron by this method.[4]

The use of aluminum to reduce boric oxide has had an interesting history. Wöhler and Deville (*5*) published a series of papers describing the preparation by this method of several crystalline modifications of what they believed to be boron, and also described well-formed crystals which were obtained from a melt of aluminum to which amorphous boron had been added. Later Wöhler (*6*) and Hampe (*7*) showed that the crystals were forms of the boride AlB_{12}. Others have verified this and have demonstrated that, although it is apparently possible to get some free boron by the use of aluminum as reducing agent, the boron is always contaminated with aluminum boride which cannot be removed. The crystal structures of the various forms of AlB_{12} have been studied (*8*) but the configurations have not been completely determined. In spite of very definite proof to the contrary, it has been the confusing general practice up to date to call this aluminum boride "crystalline boron," and it is on sale under this name.

Reduction of Compounds of Boron by Carbon, Silicon, and Calcium Carbide

Both carbon (*9*) and silicon (*10*) have been used to reduce boron compounds, but the products were badly contaminated with inert borides and purification has not been accomplished. Calcium carbide (*9*) has been tried but the purity of the product was low.

Reduction of Boron Compounds by Electrolysis

It is possible to obtain boron powder by electrolysis, and this procedure has been investigated by many workers and is covered by several patents. Andrieux has summarized (*11*) the work on this method. Fused oxide and borate baths have yielded boron when electrolyzed between metal or carbon electrodes. The production of boron, however, apparently is not a primary electrochemical process but is due to the reduction of boric oxide or borates by an active metal produced by electrolysis. For instance, in the electrolysis of molten borax, sodium is discharged at the cathode and reacts with the melt to form amorphous boron and borides. Andrieux found that the electrolysis of magnesium borate gave the best results, but the maximum boron content he obtained for the product was 92.2 per cent, and the yields were discouragingly low. As a matter of fact, this technic has led to the discovery of many new borides.

The deposition of boron by electrolysis of aqueous and non-aqueous solutions has been looked into but has not been realized (*12*). Stock and co-workers (*13*) could not obtain any boron by the electrolysis of a solution of diborane in liquid ammonia.

[4] In spite of this, some of our supply houses advertise "C.P. powdered boron." The authors have not been able to ascertain the source of this material but it seems reasonably certain that it is obtained by the Moissan method. A sample of this commercial material which the authors purchased would not react with bromine at elevated temperatures to yield boron tribromide.

Reduction of Boron Compounds by Hydrogen

The reduction of non-volatile compounds of boron by hydrogen has been tried (*14*), with negative results.

The reduction of volatile compounds of boron by hydrogen has been found to be very promising. When hydrogen is mixed with the vapor of boron trichloride or boron tribromide and the mixture is heated sufficiently, free boron and the hydrogen halides are formed. Such reactions have been initiated by passing the reaction mixture through hot tubes, or through an electric arc or the high frequency spark. Weintraub (*15*) studied these methods in detail. He passed a mixture of boron trichloride and hydrogen through a high potential alternating arc, using water-cooled copper electrodes. Boron deposited on the electrodes, fused to beads, and fell off. He reported that analysis of these beads gave 99.8 per cent to 100.2 per cent boron, with traces of silicon, but no copper or hydrogen. He did not work with the method extensively, even though it gave very pure boron, because it was possible to prepare only small amounts of the element. Many others, including Kroll (*16*) and Kahlenberg (*17*), also report the preparation of pure boron by this method, the latter claiming to have secured massive chunks, which he stated were not crystalline. Although the arc method has been reported on so favorably by several workers it seems likely that there is great danger of serious contamination of the boron by the electrode material.

Another method of carrying out the reduction of the boron halides by hydrogen, which has given very good results, is to pass the mixture over a filament or rod heated electrically. The filament must be made of a substance inert toward boron at the temperatures necessary for the reduction. Carbon and many metals are unsatisfactory for heating units because of serious boride formation. Tungsten filaments have been used by several investigators with success. Warth (*18*) found that tungsten could be used up to 1850°C. before it reacted with the boron. Layers of boron several millimeters thick have been secured by this method and some evidence of crystallinity has been observed (*19*).

The reduction of boron trichloride by hydrogen activated by passing the gaseous reaction mixture over hot catalysts such as powdered nickel or charcoal has been studied (*20*) and was found to proceed below 500°C., but the yields of boron were very poor and separation of boron from the catalyst was difficult.

Thermal Decomposition of Compounds of Boron

Boron compounds undergo thermal decomposition if the temperature is high enough, massive boron being produced at very high temperatures, powdered boron at lower temperatures The great difficulty is to carry out such thermal decomposition without getting reaction with the container and other parts of the apparatus. Solid compounds of boron have been decomposed by heating them in boats or crucibles. Boron nitride was found to decompose (*9*) when heated in a graphite boat in a graphite tube at 2450°C. but the boron liberated combined with the graphite to form boron carbide. Many investigators have tried to convert powdered Moissan's boron to massive boron by fusion or sintering. At the high temperatures used, the compounds of boron contaminating the element, notably magnesium boride, are said to dissociate and the elements others than boron vaporize. This is believed to accomplish some purification so that boron 98 per cent pure can be obtained. Weintraub (*15*) heated Moissan's boron in a high potential arc. The sample was supported in a copper cup which formed one electrode and the other electrode was of copper and was water-cooled. The electrodes were supported in a glass vessel filled with hydrogen. Weintraub mentions melting several pounds of boron which was 97 to 98 per cent pure. He also developed an arc furnace employing a boron nitride container in which boron rods could be formed. Tiede and Birnbräuer (*21*) heated Moissan's boron in a cathode ray vacuum furnace and stated that the element underwent purification and melting. The massive boron obtained by these methods was hard and brittle and had a conchoidal fracture.

Volatile compounds of boron such as the halides and the hydrides have been decomposed by passing their vapors through an arc or by bringing them in contact with a hot surface or filament. Boron of high purity is reported procurable by this method, but it is either a very fine powder or of vitreous structure.

PROPERTIES REPORTED FOR BORON

The properties of boron have been studied by many workers. In most cases the purity of the samples used seems to be very doubtful and the properties reported undoubtedly are not accurate. This is especially true for the powdered boron. The properties reported for only the massive material will be summarized here. The black solid has a metallic luster, and both vitreous and polymicrocrystalline forms have been described. Conchoidal fracture is frequently noticed. Its density (*22*) is $2.33 \pm 0.01^{20°C.}$ There is general agreement in the literature that boron is harder than the sapphire but softer than the diamond, and Mellor and his coworkers (*19*) were able to scratch carborundum with boron. The melting point is probably near 2200° ± 100°C. (*21*). Boron is diamagnetic, its susceptibility$^{20°C.}$ being 6.7×10^{-6} (*23*). The electrical conductivity of boron is not known with certainty, the data reported being very conflicting. Weintraub (*15*) reported for boron, prepared by the sintering of "Moissan's boron," a very low conductivity of 1.7×10^{-6} reciprocal ohms at 23°C. and a large positive thermal coefficient, the conductivity increasing a million fold when the temperature was raised to 600°C. He also reported a resistance breakdown effect. Other measurements indicate a much smaller temperature effect and suggest that impurities or other crystal imperfections might have been responsible for Weintraub's data. These data, however, have stimulated a great amount of research in an effort to exploit this interesting electrical behavior.

The chemical behavior of massive boron has not been studied extensively. It is inert toward water and toward hydrochloric and hydrofluoric acids of all concentrations at their boiling points. It is rapidly oxidized to boric acid by nitric acid. It reacts rapidly with chlorine and bromine above 400°C. There are very little thermochemical data available.

X-RAY STUDIES OF BORON

It is unfortunate that most of the investigations of boron were made before X-rays came into use for the study of the structure of solids. Most of what seem to have been the best samples of boron, from the standpoint of purity and crystallinity, were not examined by X-ray methods. The few cases of X-ray studies described in the literature (*19, 22*) involve only powder X-ray diffraction patterns, because no single crystals have been available. It has been impossible to interpret these photographs because of their complexity, and the patterns reported do not agree. They do show that the samples studied were either vitreous or very finely polycrystalline in character.

RESEARCH IN PROGRESS

For several years investigations have been in progress in the Cornell laboratories with the purpose of preparing boron in pure crystalline form, preferably as single crystals, determining its characteristic X-ray diffraction pattern, and solving the problem of the crystal structure of the element.

Single crystals of appreciable size, believed to be of high purity, have been produced by the reduction of boron tribromide at the surface of hot tungsten or tantalum filaments. The factors affecting the development of crystals are being studied and a comprehensive investigation of the properties of pure boron is underway.

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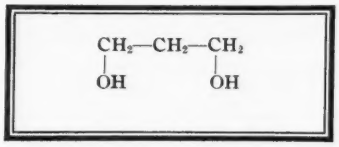
FORMULA OF THE MONTH



PROPYLENE GLYCOL

Experiments indicate that this substance may have antiseptic action toward air-borne infectious agents.

There are 30 shots at the enemy in a set of brass curtain fixtures; the metal they contain would produce that many cartridges for a soldier's rifle.

When a tanker loaded with gasoline is sunk by an Axis submarine enough gasoline is lost to have driven 5000 autos for a whole year at the normal rate.

If you find electric fans are scarce this summer, consider that the copper from a dozen such fans is enough to provide all the copper needed in fabricating a 20-mm. aircraft cannon to make it hot for the Japs and Nazis.

The Future of Electroforming

L. ASHLEY RICH *Hillyer Junior College, Hartford, Connecticut*

INDUSTRY can look for revolutionary changes in the method of manufacturing wire screen and complicated flat metallic objects. Ten years from now there will probably be little screen made by weaving wire. Continuous rolls of screen as well as small, identical objects are being turned out now by a new process not yet described in the literature. Based on electroforming of metal on a continuously rotating cylinder, practically no labor is involved except in the manufacture of the rolls upon which electrodeposition takes place.

In the present war situation many products of this process are of primary importance. Thus, bomb sight parts, fine screen up to 400 mesh, air filters for carburetors, nickel screens for Fourdrinier machines, have tremendous defense value. All of these items and many others are being made now. We may have to wait until peace comes to see more general application of the process.

For this reason, cloth printed by means of screen-rolls, made by a modification of this process, may not come into common use for the duration. After the war, however, we must be ready for radical changes due to the use of materials and machine parts made automatically by electroforming. Continuous electrodeposition of metal on rollers from plating baths made from scrap copper and nickel will be an important new industry. It is obvious from what has been done already that these new automatic electroforming methods conserve scrap copper and nickel and save a tremendous amount of trained manpower.

The machines now used for this work have been brought to a considerable degree of perfection for continuous operation. Nevertheless, future needs will demand that the work be so greatly expanded that existing facilities can only be considered to be a research pilot plant for this new industry.

In the making of the rollers on which the electroforming of screen is accomplished, there is still much handwork required. Briefly, the following steps are involved in the manufacture of the matrix for an 80-mesh screen:

An accurately ruled glass plate is placed over a piece of copper coated with lithographer's glue, ammonium bichromate, and albumisol. This copper lithography process results (after developing, baking, and washing) in a cross hatch of fine lines on the copper. These lines will not plate with copper, but the background will build up. Electroplating this copper plate therefore makes the background stand up in relief. The next process is to make a cylinder of this copper plate with these lines inside. Seams have to be made carefully so that no blemish will show in the final screen.

Next, on the inside of this copper cylinder, a heavy nickel coating is deposited. This has to be about one-eighth of an inch thick as it constitutes the cylinder which rolls over in the plating machine and from which the screen is peeled. The outside copper is now dissolved by submerging the cylinder in a tank of chromic acid. The nickel cylinder now has in relief the cross hatch corresponding to the screen wanted.

This nickel core is then reinforced and coated with a plastic product (Heresite). When this is baked, it completely covers the nickel. It is sanded down carefully by hand so that the resulting smooth-surfaced cylinder has a webbing of nickel lines interspaced by plastic. Obviously, copper will plate now on the nickel and leave open spaces corresponding to the plastic areas. The product need not be screen; it can be any design with open and closed areas, since a photographic positive could have been used instead of the original glass plate.

Most master cylinders for screen manufacture are about 30 inches wide and 12 inches in diameter. Before inserting the cylinder in the screen-plating machine the roller is lightly chrome plated. This has to be done frequently in order to prevent the deposited screen from adhering to the cylinder.

In the plating machine the lower half of the rotating cylinder dips in the copper sulfate bath. This bath is supplied by a tower filled with scrap copper screen through which the copper sulfate is circulated. A blower forces air up through the tower.

As the cylinder slowly revolves, it is waxed by a rapidly rotating roller brush. As the cylinder rotates, its lower half which dips below the bath becomes plated, since the roller cylinder is the cathode. At the top of its revolution the screen or other plated coating is peeled off and rolled up.

This screen frequently has to be built up with copper or nickel. In another machine for this purpose the screen is first run through a phosphoric acid stripping bath. This etches out the open spaces in the screen. A washing device then cleans it while it runs through an atmosphere of illuminating gas.

The screen is now built up to the desired thickness by running it through a nickel sulfate bath. Of course, adequate provision is made for maintenance of these baths with provisions for testing, continuous circulation, filtration, addition of wetting agents and other materials.

The product is far stronger than woven screen. These screens are capable of taking the beating such machines as the Fourdrinier paper machine can give them.

A slightly more intricate process is involved in the manufacture of cylindrical rollers by means of which floc or other cloth printing processes can be achieved.

A six-foot-long cylinder of the type described, whose cross section is dumb-bell shaped, is plated in nickel. This coating, because of the shape of the cylinder, can be stripped off as a complete perfect screen. It is now built up heavier in nickel. A ceresin-paraffin mixture of waxes is used to fill all the pores of this nickel screen and the excess is scraped off, leaving the nickel clean.

Coating the cylinder with graphite and overlaying

(*Continued on page 392.*)

Uses of Microörganisms in the Production of Chemical Products

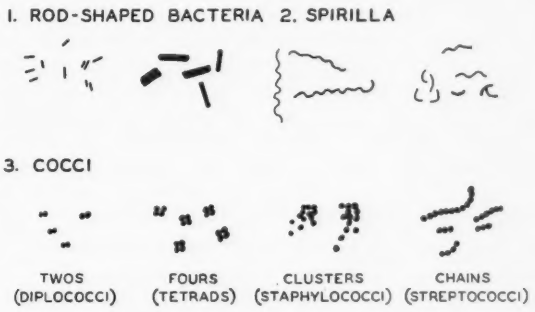
CECIL G. DUNN[1] *Office of the Quartermaster General, Washington, D. C.*

BACTERIA, yeasts, and molds, referred to as microörganisms on account of their small size, are important chemical reagents.

Microörganisms are used in the manufacture of certain chemical and food products in preference to purely chemical methods for several reasons. Some chemical products may be made more cheaply by the action of microörganisms on inexpensive carbohydrate materials (which in some instances are waste products) than from other chemical compounds. In many cases microörganisms produce chemical compounds which have not been synthesized in the laboratory, or which may be made only with great difficulty. Sauerkraut, pickles, cheese, and other food materials are changed in appearance, flavor, and consistency by microorganisms. These complex changes would, in most cases, be impossible to duplicate by chemical means alone. Alcoholic beverages, for example, cannot be produced synthetically in a satisfactory manner.

There are thousands of species of bacteria, yeasts, and molds. A relatively few cause diseases in plants or animals, but most are apparently harmless to man. Some of the latter are extremely valuable, since they are used in the production of chemical agents of importance, desirable food products, and biologically useful materials.

We are concerned primarily with microörganisms which are of value in the fields of medicine, agriculture, and industry, because of some special chemical activity. In medicine bacteria may be used to produce life-saving vaccines and various drugs. Penicillin, a substance formed by a mold, is a germicide. In agriculture bacteria are instrumental in carrying out many desirable transformations. Certain species of microörganisms have the ability to fix atmospheric nitrogen; other species transform this nitrogen into ammonia; still others change the ammonia to nitrites, and the nitrites to nitrates. From the nitrates green plants get their supply of nitrogen. These nitrogen-fixing bacteria, then, are natural fertilizers. The dead organic matter of leaves and animals is broken down into simpler compounds by bacteria, which solves an important disposal problem for man. Fungi (basidiomycetes) are the chief agents for decomposing fallen timber. To the entomologist, also, bacteria are a valuable tool, since they destroy insects.



VARIOUS TYPES OF BACTERIA

Microörganisms are particularly important in industry, where the food technologists use them in the preparation of such food materials as vinegar, pickles, sauerkraut, butter, cheese, acidophilus milk, and a large number of other fermented products. In each case the bacteria, yeasts, or molds bring about changes in the food materials which may be highly desirable. For example, in the manufacture of Roquefort cheese, both bacteria and molds play an active part. This particular cheese is classified as a mold cheese, since its characteristics are due mainly to changes which have been brought about through the action of the mold.

Although certain species of microörganisms produce desirable changes in foods, there are others which bring about very undesirable changes. Oranges and apples in storage are destroyed primarily by molds. If a loaf of bread is permitted to stand in a warm, moist room, it soon becomes covered with mold growth. Meat, unless preserved, is attacked by bacteria and decomposed, giving rise to a very offensive odor. Un-

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pasteurized milk, when allowed to stand at room temperature or above, soon becomes sour.

Since we are here primarily concerned with the uses of microörganisms in the manufacture of chemical products, some of the fundamental concepts of fermentation should be briefly discussed.

PRINCIPLES OF FERMENTATION

The nature of the microörganism and the conditions of fermentation will in each case determine the kinds and quantities of the end-products.

Selection of the Microörganism

Although there are frequently several species of bacteria, yeasts, or molds, which have the ability to produce a particular chemical substance, there is usually one certain species or strain which has the ability to produce the highest yields. Molds are outstanding for their ability to produce acids; yeasts, for alcohol production; and bacteria for acids and the higher alcohols. It is thus very important to select the right microörganism for the formation of the desired chemical product.

Conditions of Fermentation

There are certain conditions, in addition to the selection of the microörganism, which must be satisfied in order to obtain high yields of the desired chemical product. These include the selection of a suitable raw material; the use of this raw material in the correct concentration; nutrient salts or special food substances, if the raw material is deficient or lacking in certain materials; satisfactory pH, temperature, and oxygen relationships; the absence of inhibitory agents such as direct sunlight.

1. The raw material, which may be molasses, fruit juices, grains, such as corn, wheat, or rice, starches, sugars, alcohols, acids, salts, etc., must be one which the microörganisms can ferment. Furthermore, it must be adjusted to the proper concentration by the use of water. Concentrations of 2 to 15 per cent are commonly used.

2. When pure sugars, starches, or certain other substances are used as raw materials, it is also essential to provide nutrient salts or special food substances, for microörganisms, like human beings, require definite elements for growth. These elements include carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, potassium, magnesium, and others, which are supplied as salts. In each fermentation the selection of the salts which give the best results and the use of the optimum concentration of each are necessary if high yields are to be expected.

3. The intensity of acidity or alkalinity, technically referred to in terms of pH, must be adjusted properly.

4. There is an optimum temperature for the growth of each organism and for each particular fermentation, although the best temperature for growth may not coincide with that best for the fermentation.

5. It is almost always necessary to sterilize the raw materials, before they are inoculated (seeded) with the microörganisms. Various other bacteria, molds, or yeasts may be present and, unless they are destroyed, will utilize the food materials with the production of undesired end-products.

6. The sterilized nutrient mash is inoculated with a pure culture of the selected microörganism and incubated at the temperature most favorable for the fermentation.

7. The chemical activity of the bacteria, yeasts, and molds is due principally to the enzymes which they secrete. Enzymes are organic catalysts, the reactions of which are influenced by the nature of the materials present, their concentrations, the temperature of the medium, the pH, and other conditions. The action of microörganisms upon sugars, starches, and other food materials may be likened to digestion. In general, simple products are formed from complex ones and soluble from insoluble ones. But this is not invariably true, for substances much more complex than the original ones—and even insoluble compounds—are sometimes produced by microörganisms.

8. The desired products, formed thus by the biochemical action of the microörganisms, are then separated by fractional distillation or by chemical means.

CHEMICAL ACTIVITY OF THE BACTERIA

Bacteria are single-celled plants of extremely small size. An isolated bacterial cell may be so small that it would require 25,000 such cells, placed end to end, to make a line one inch long. The rate of reproduction of the bacterial cell is important for, under optimum conditions, the cell may divide with the formation of two new cells in 20 minutes or less. Each new cell may give rise to two more, and so on. The total number of bacteria, however, is limited by the available food materials, the accumulation of waste products, and other factors.

Butanol-Acetone Fermentation

Butanol (butyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$), acetone ($CH_3{\cdot}CO{\cdot}CH_3$), and ethyl alcohol ($CH_3{\cdot}CH_2{\cdot}OH$), are produced in the ratio of 6:3:1 from sterilized corn, molasses, or other starchy or sugary materials by spore-forming bacteria, such as *Clostridium acetobutylicum*. The fermentation is carried out at temperatures of 98.6° to 107.6°F. and requires two to three days for completion. The butanol, acetone, and ethyl alcohol are separated from the mash by distillation and from each other by fractional distillation. Butanol is used in manufacturing lacquers, photographic films, penetrating oils, synthetic resins, and for many other purposes; acetone is important in the manufacture of plastics, cellulose acetate silk, photographic film, smokeless powder, etc.

Fermentations by the Acetic Acid Bacteria

As a group, acetic acid bacteria are very active biochemically. Various members of this group have the ability to produce acetic acid and vinegar, sorbose,

gluconic acid, and a large number of other compounds from suitable nutrient sources under controlled conditions. This group of bacteria is particularly noted for its oxidizing ability.

Vinegar is the product made by the alcoholic and subsequent acetous fermentations of various sugary or starchy materials, such as apple juice, grape juice, barley malt, and cereals, the starch of which has been converted to sugar by malt. In the manufacture of vinegar from apple juice, for example, the sugars are fermented by yeast with the production of ethyl alcohol ($CH_3 \cdot CH_2 \cdot OH$), carbon dioxide gas (CO_2), and small amounts of glycerol, acetic acid, and other chemical products. The alcoholic fermentation is usually brought about by yeast cells which are present on the skin of the crushed apples. After the completion of the alcoholic fermentation acetic acid bacteria ferment the ethyl alcohol, with the formation of acetic acid.

There are several methods for producing vinegar, or acetic acid. One of the modern methods for large scale production is to allow the solution containing alcohol (usually apple cider or wine acidified with a small quantity of vinegar), to trickle down over beechwood shavings (or other suitable materials such as coke or rattan) which are seeded with many millions of acetic acid bacteria. As it passes over the shavings, the alcohol is oxidized to acetic acid by the bacteria. An abundance of oxygen is essential for this process. Temperature control is also important, since too high a temperature results in loss of the volatile alcohol and acetic acid. Temperature, air circulation, and flow of the alcohol-acid mixture are automatically controlled in a vinegar generator designed by Heinrich Frings in 1937.

In the manufacture of vitamin C, which is now becoming so important, a certain sugar-like compound, called *sorbose*, is used. This is produced from the alcohol, sorbitol, by bacterial action.

Lactic Acid Fermentations

Lactic acid production by bacteria is utilized in several ways.

Lactic acid ($CH_3 \cdot CHOH \cdot COOH$) may be manufactured from whey, molasses, corn sugar (glucose), or other carbohydrate materials by the use of such lactic acid bacteria as *Lactobacillus bulgaricus* and others. The acid is separated from the mash and purified by chemical means. Lactic acid and its derivatives have many important uses in the pharmaceutical, food, and chemical industries; for example, in the acidification of confectionery, fruit juices, lemonades, pickles, in the manufacture of plastics, in the dyeing of silks, in vegetable tanning, and as a solvent.

Sauerkraut is a fermented product made by shredding cabbage, mixing two to three per cent of salt with the shreds, applying pressure to aid in the extraction of juices from the shreds, and allowing fermentation for a period of three to four weeks. Lactic acid fermentation takes place and the product then has the characteristic flavor and appearance of sauerkraut. The lactic acid produced aids in the preservation of the product.

Silage is a product made by grinding up corn, alfalfa, or other materials, placing the ground substances in a silo, adding salt, and permitting fermentation to take place. Lactic acid, ethyl alcohol, and other chemical compounds are produced when the sugars present in the vegetable material are acted upon by lactic acid bacteria and yeasts.

In the manufacture of various pickles and olives, lactic acid fermentation plays an important part in producing certain of the characteristics of the final product.

There are a number of fermented milk products which are prepared from the milks of various animals: the cow, ewe, goat, and mare. Some are made from pasteurized milks which have been inoculated with special types of lactic acid bacteria. Acidophilus milk is a special product used in the treatment of intestinal disorders. It is made by inoculating sterilized milk with a culture of *Lactobacillus acidophilus* and incubating at body temperature (98.6°F.) until the proper degree of acidity has been produced. *Kefir* is a fermented product made by seeding milk with kefir grains. These grains usually contain lactic acid bacteria, a lactose-fermenting yeast, and other microörganisms. *Kumiss*, *yoghurt*, and *leben* are other fermented milks. Some contain small amounts of ethyl alcohol in addition to lactic acid.

Lactic acid bacteria are used also in the manufacture of butter and cheese.

Miscellaneous Uses of Bacteria

The extract from corn fermented by *Clostridium acetobutylicum* (the butanol-acetone organism) is a rich source of riboflavin (vitamin G or B_2). It also contains variable quantities of pantothenic acid, vitamin B_1 (thiamine), vitamin B_6 (pyridoxine), and biotin.

Bacteria of a group related to *Bacillus subtilis* (referred to as the hay bacillus) are used for the manufacture of enzymes known as amylases and proteases. These enzymes are used commercially when it is desired to break down starches and proteins, respectively.

Since certain lactic acid bacteria require riboflavin for growth and since the amount of growth is directly proportional to the amount of riboflavin in the medium, it is thus possible to estimate the quantity of this vitamin present. To do this, the growth or acid production of *Lactobacillus casei* in the medium being tested is compared with its growth in a medium with a known riboflavin content.

Certain types of bacteria may be used to detect the presence of oil in possible oil-bearing strata of the earth's crust.

There are many other industrial uses of bacteria where their biochemical activities are of much value, for example, in the retting of flax and in the stabilization of sewage.

Table 1 lists some of the more common compounds formed by bacteria.

CHEMICAL ACTIVITY OF THE YEASTS

The yeasts, like the bacteria, are one-celled microorganisms. They average slightly larger than the bacteria in size and reproduce principally by a process known as budding. They do not ordinarily reproduce so rapidly as bacteria, nor do they form heat-resistant spores. Almost all of the yeasts of commercial importance are species of the genus *Saccharomyces*.

TABLE 1

PRODUCTS OF BACTERIAL FERMENTATION*

Fermentation Product	*Materials from Which Formed*	*Organisms Causing Change*
Acetaldehyde	Sugars, ethanol, pyruvic acid, etc.	Acetic acid and butanol-acetone bacteria; *Escherichia coli*, etc.
Acetic acid	Ethanol, glucose, cellulose, etc.	Acetic acid, heterofermentative lactic acid, butanol-acetone, isopropanol, propionic acid, and cellulose-fermenting bacteria; *E. coli*
Acetoacetic acid	Acetic acid	Butanol-acetone bacteria
Acetone	Starch, sugars, acetoacetic acid, acetic acid, isopropanol	Butanol-acetone, ethanol-acetone, isopropanol, and acetic acid bacteria
Acetylmethylcarbinol	2:3-butyleneglycol, sugars, pyruvic acid, etc.	*Aerobacter aerogenes*, butanol-acetone and acetic acid bacteria
Butanol	Starch, sugars, butyric acid, etc.	Butanol-acetone and isopropanol bacteria
Butyric acid	Starch, sugars, cellulose, acetic acid, etc.	Butyric acid and cellulose-fermenting bacteria
2:3-butyleneglycol	Glucose, diacetyl	*A. aerogenes*
Carbon dioxide	Starch, sugars, etc.	Butanol-acetone, *A. aerogenes*, *E. coli*, and many other bacteria
Dihydroxyacetone	Glycerol	Acetic acid bacteria
Ethanol	Sugars, starch, cellulose, acetaldehyde, etc.	*Termobacterium mobile* Lindner, butanol-acetone, ethanol-acetone, heterofermentative lactic acid, and cellulose-fermenting bacteria; *E. coli*, etc.
Formic acid	Glucose, cellulose, etc.	Butyric, cellulose-fermenting bacteria; *E. coli*, etc.
Fructose	Mannitol	Acetic acid bacteria
Galactonic acid	Galactose	Acetic acid bacteria
Galactose	Dulcitol	Acetic acid bacteria
Gluconic acid	Glucose	Acetic acid bacteria
Glycerol	Glucose, etc.	Heterofermentative lactic acid bacteria
Glycerophosphoric acid	Triosephosphoric acid	Lactic acid bacteria, *E. coli*
Hexosediphosphate	Glucose	Lactic acid bacteria, *E. coli*
Hydrogen gas	Glucose, lactose, etc.	Butyric acid bacteria, colon-aerogenes group, and other bacteria
Isopropanol	Starch, sugars	Isopropanol-acetone bacteria
2-Ketogluconic acid	Gluconic acid (glucose)	Acetic acid bacteria
5-Ketogluconic acid	Gluconic acid (glucose)	Acetic acid bacteria
Kojic acid	Glucose, fructose, etc.	Acetic acid bacteria
Lactic acid	Starch, sucrose, glucose, fructose, etc.	Lactic acid, propionic acid, and cellulose-fermenting bacteria; *E. coli*, etc.
Mannitol	Fructose	Heterofermentative lactic acid bacteria
Mannonic acid	Mannose	Acetic acid bacteria
Mannose	Mannitol	Acetic acid bacteria
Methylglyoxal	Sugars, hexosediphosphate, etc.	Acetic acid, butanol-acetone, lactic acid, and propionic acid bacteria; *E. coli*
Phosphoglyceric acid	Sugars, hexosediphosphate	Lactic acid bacteria, *E. coli*
Propanol	Propionic acid	Butanol-acetone bacteria
Propionic acid	Glucose, propanol, lactic acid, glycerol, pyruvic acid	Propionic acid and acetic acid bacteria
Propionaldehyde	Glucose, glycerol	Propionic acid bacteria
Propylene glycol	Rhamnose	*Bact. rhamnosifermentans*
Pyruvic acid	Sugars	Butyric, lactic, and propionic acid bacteria; *E. coli*
Sorbose	Sorbitol	Acetic acid bacteria
Succinic acid	Glucose, fructose, lactose, and other sugars	Propionic acid bacteria, *E. coli*, etc.

* Reprinted by permission from PRESCOTT AND DUNN, "Industrial microbiology," McGraw-Hill Book Company, Inc., New York City, 1940.

The yeasts are best known for their action on sugars to form ethyl alcohol and carbon dioxide in almost equal quantities, along with small quantities of acetic acid, glycerol, and traces of the higher alcohols (produced from proteins). The reaction may be expressed as follows:

$$\underset{\text{sugar}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethyl alcohol}}{2C_2H_5OH} + \underset{\text{carbon dioxide}}{2CO_2}$$

This reaction shows only the raw material and the principal end-products, although the process is very complicated, involving many intermediate reactions. Conditions favoring the fermentation are the presence of suitable sugars, nutrient materials, an acid reaction, and a temperature of approximately 86°F.

Ethyl alcohol (known also as industrial, grain, power, or fuel alcohol), a product with a multitude of important chemical uses, is produced commercially by fermentation, principally from molasses, a low-priced raw material which contains sugars, proteins, mineral matter, and other ingredients. Starches may be hydrolyzed to sugars by molds (by the Amylo process), by mold enzymes, by malt, or by acids; and the sugars fermented to ethyl alcohol by the yeast.

The carbon dioxide gas evolved during the fermentation is collected, washed, freed of impurities, compressed, and used to form dry ice or for various other purposes.

Beer, ale, wine, rum, whiskey, and cider are beverages produced by alcoholic fermentations.

Glycerol, a chemical product with many uses, may be produced by the fermentation of nutrient sugar solutions when the medium is made alkaline. Selected strains of yeasts (usually *Saccharomyces ellipsoideus*) are used and the temperature is carefully controlled.

Compressed yeast may be made in a number of different ways, using different raw materials such as molasses and ammonia, cereal grains, or sugars and nutrient salts. In each process, it is important to supply a large amount of oxygen (air) to the mash, adjust the acidity to a pH of about 4.4, and maintain a temperature favorable for the growth of the yeast. The yeast is separated from the mash by centrifuging, washed, and compressed into cakes.

Bakers make use of yeast in causing bread dough to rise. Yeast ferments the sugars present in the dough, producing ethyl alcohol and carbon dioxide. Ethyl alcohol is lost by evaporation before and during the baking process. The carbon dioxide gas is trapped in the dough by the proteins of the flour and the dough becomes "light." Thus, the gas is the important fermentation product in this case.

Yeast is an excellent source of the vitamin B complex which is so important in human nutrition. In the complex may be found the chemical agents thiamine (vitamin B_1), riboflavin (vitamin G or B_2), pyridoxine (vitamin B_6), pantothenic acid, and niacin. Selected

yeast is grown under carefully controlled conditions in order to obtain the highest yields of these vitamins. The yeast may then be incorporated in bread, peanut butter, or other food materials in order to enrich them with the B complex.

Yeast also contains ergosterol, a substance which, when irradiated with ultra-violet light, forms vitamin D. By feeding cows irradiated yeast, the vitamin D content of the milk may be increased.

Certain enzymes may be extracted from yeasts and used commercially. One such enzyme, known as invertase, is used in making candies. This substance acts upon sucrose (cane sugar) to break it down to the simpler sugars—glucose and fructose, which, together, are sweeter than the original sugar and crystallize less easily.

During World War I, the Germans and Russians used *Endomyces vernalis*, a yeast, as a source of fat and protein, on account of the great difficulty they had in getting enough of the usual fats. Various food materials have been made from this and other yeasts.

CHEMICAL ACTIVITY OF THE MOLDS

The molds are more complex than either the bacteria or the yeasts. There are thousands of different species. From an industrial point of view, species of the genera *Aspergillus*, *Penicillium*, and *Rhizopus* are most important. Molds are of various colors—black, gray, green, blue, yellow, etc., the color being due in most cases to the "fruiting bodies." Molds reproduce principally by means of spores of which there are various types. While these are not so resistant to heat as bacterial spores, they are especially resistant to drying and are easily carried through the air on account of their light weight.

A large number of chemical products may be manufactured by molds (refer to Table 2), but the most valuable mold fermentations are those in which citric and gluconic acids are produced.

Millions of pounds of *citric acid* are produced annually by fermentation. The raw materials are usually sucrose, technical glucose, maltose, and molasses. Nutrient salts, such as ammonium nitrate, potassium hydrogen phosphate, and magnesium sulfate, are added to the medium to supply essential minerals for the growth of the molds and to favor a maximum yield of citric acid. The medium is made strongly acid, and the sugar and nutrient salts, all in proper concentrations, are sterilized in shallow pans, cooled, and inoculated with the spores of the mold selected, for example,

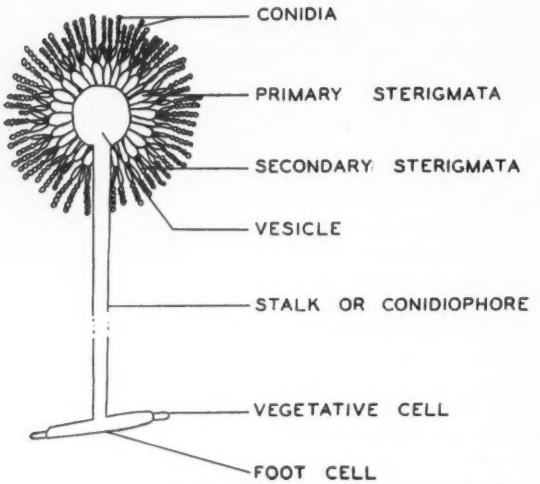
TABLE 2

SOME PRODUCTS FORMED BY MOLDS

Acids	*Alcohols*	*Enzymes*	*Pigments*	*Polysaccharides*	*Sterols*	*Miscellaneous*
Acetic	*i*-Erythritol	Amidase	Aspergillin	Capreolinose	Cholesterol	Acetaldehyde
Aconitic	Ethyl	Amylase (α and β)	Aurantin	Galactocarolose	Ergosterol	Alboleersin
Allantoic	Glycerol	Carboxypoly-peptidase	Aurofusarin	Glycogen	Fungisterol	Dimethyl selenide
Byssochlamic	Mannitol	Catalase	Auroglaucin	Luteic acid	Phytosterol	Ergot
Carlic		Cellobiase	Boletol	Mannocarolose		Ergosteryl palmitate
Carlosic		Cytase	β-Carotene	Mycodextrin		Ethyl acetate
Carolic		Dextrinase	Catenarin	Rugulose		Gums
Carolinic		Dipeptidase	Chrysogenin	Starch (mold)		Hydroxylamine
Citric		Emulsin	Citrinin	Trehalose		Lipins
3,5-Dihydroxyphthalic		Erepsin	Citromycetin	Varianose		Luteoleersin
Dimethylpyruvic		Gentianase	Cynodontin			Palitantin
Formic		Gentiobiase	Emodin mono-methyl ether			Phenylethylamine
Fulvic		α-Glucosidase	Erythroglaucin			Terrein
Fumaric		β-Glucosidase	Flavoglaucin			Vitamins
Fusarinic		Histozyme	Fulvic acid			Arsenic compounds: Methyldiethylarsine Dimethylallylarsine Trimethylarsine, etc.
Gallic		Inulase	Helminthosporin			Chlorine-containing compounds: Erdin Geodin Griseofulvin
Gentisic		Invertase	Hydroxyisohelmin-thosporin			
Glaucic		Lactase	Monascoflavin			
Glauconic		Lecithinase	Monascorubin			
d-Gluconic		Lipase	Ochracin			
Glucuronic		Maltase	Oösporin			
Glycolic		Melezitase	Phoenicin			
Glyoxylic		Nuclease	Physcion			
2-Hydroxymethyl-furane-5-carboxylic		Protease	Ravenelin			
Isovaleric		Raffinase	Rubrofusarin			
Itaconic		Rennet	Tritisporin			
Kojic		Sulfatase				
γ-Ketopentadecoic		Tannase				
Lactic		Trehalase				
Luteic		Urease				
Malic		Zymase				
d-Mannonic						
l-γ-Methyltetronic						
Methyl salicylic						
Minioluteic						
Mycophenolic						
Oxalic						
Penicillic						
Puberullic						
Pyruvic						
Spiculisporic						
Succinic						
Terrestric						

* Reprinted by permission from PRESCOTT AND DUNN, "Industrial microbiology," McGraw-Hill Book Company, Inc., New York City, 1940.

Aspergillus niger, a mold with black spores. The pans are incubated at 82° to 86°F. for about 10 days, after which the citric acid is separated as calcium citrate and purified. After the addition of a calculated amount of sulfuric acid, and filtration to remove the precipitated calcium sulfate, citric acid is obtained. This acid has many uses, especially in the food and pharmaceutical industries.



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Aspergillus (DIAGRAMMATIC)*

* Adapted from THOM AND CHURCH, "The Aspergilli," The Williams and Wilkins Company Baltimore, 1926.

Gluconic acid is made by bubbling air through nutrient solutions of glucose, which have been inoculated with the same mold, *Aspergillus niger*. Only a few hours are required. Gluconic acid is a cleaning agent, while its calcium salt is used as a drug.

Gallic acid may be prepared from moist tannin or tannin extracts through the action of a species of *Aspergillus*. Gallic acid is used in the manufacture of inks and of dye substances, and as a pharmaceutical.

There are four main types of enzymes formed by molds which are used industrially. These include amylases, which convert starches to dextrins and sugar, and which are used for such purposes as the desizing of textiles; invertase, which converts sucrose (table sugar) to glucose and fructose, and which may be used to produce soft centers in chocolates; proteases, which change complex protein molecules to more simple ones, and which may be used to remove the gum from silk and the hair from hides; and pectinase, an enzyme which attacks pectin materials and which may be used in the clarification of fruit juices.

Soy sauce, a base for table sauces, tamari sauce, and miso are products made from soy beans by fermentations. Molds play an important role in the production of the final appearance, odor, and flavor.

THE FUTURE OF ELECTROFORMING

(*Continued from page 386.*)

it with a $^1/_{16}$-inch thick continuous copper deposit now completes a solid cylinder of copper free from holes and with a firmly attached strong nickel screen beneath it.

This copper roll is now glue-bichromate coated, greased, and covered with photographic film having on it the design wanted on the cloth. Arc lighting exposes the copper and it is developed, baked, and washed. The copper cylinder is now plated over with copper and nickel which cover all except the exposed designs on the copper cylinder. As a result the cylinder can now be immersed in chromic acid and carefully etched. Only the designs are attacked; the copper covering only is dissolved; and these designs have the firmly attached underlying nickel screen to support them. There is therefore no chance of the usual difficulties in printing from such rollers and many miles of cloth have been run from a single roller of this type. In fact, after printing the cloth, these rollers can be returned and a new design put on them simply by stripping the copper, replating, photographing on it, and etching in the new designs.

Close observers will notice a change in our mast-head page this month, a new assistant to the editor. Miss Marilyn Evans came to the JOURNAL from Wellesley College just two years ago, when a new editorial staff took over. She leaves us as Mrs. John P. Howe. The standard of the JOURNAL during the two intervening years was in no small part the result of her conscientious and painstaking efforts. A new editor, with no experience, could scarcely have had a more competent assistant. Our best wishes go with her.

Miss June Billhardt comes to us from Mount Holyoke College, where she specialized in chemistry. She takes over a position for which a high standard has already been set.

Out of the Editor's Basket

AN IMPORTANT announcement made recently by the War Production Board says that . . . because of the critical shortage of scientific equipment, university and other private laboratories engaged in research work unrelated to the production of materials, or in other research not directly connected with the war effort, will be unable to secure new laboratory equipment unless the particular use is approved by the Director of Industry Operations.

"In addition to making special provision for the handling of requests for equipment for uses not specifically permitted, the order permits any laboratory or other user to obtain repair parts and operating supplies for maintenance of existing equipment and activities.

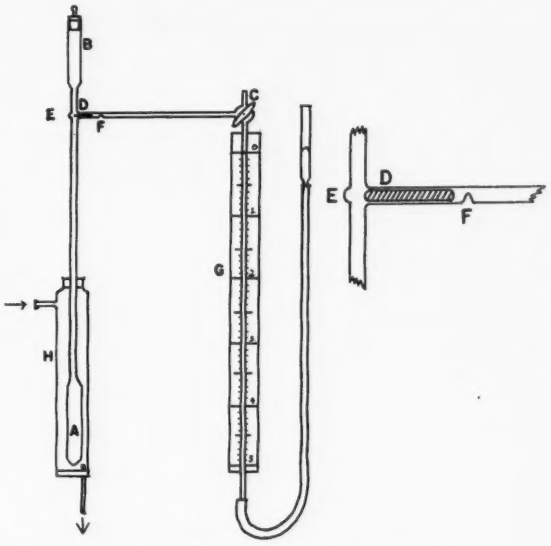
"The regulations, which will affect 600 manufacturers and 3000 laboratories, prohibit the sale, delivery, renting, or purchase of laboratory equipment in which any of the following materials are contained: aluminum, chromium, copper, iron, magnesium, molybdenum, nickel, steel, tantalum, tin, titanium, any alloy of these metals, rubber, any synthetic rubber, or non-cellulose base synthetic plastics.

"In order to buy or sell laboratory equipment containing the above materials, a certification must be made by a duly authorized official of the purchasing company or laboratory stating that the equipment will be used only for one of the following purposes:

1. Research on, or analysis of, materials.
2. Research by or for Government agencies or "Lend-Lease" countries.
3. For training of personnel for the Army and Navy or other Government Departments or Lend-Lease countries.
4. To the extent necessary for the replacement of existing essential equipment and activities in laboratories.
5. To the extent necessary for repair parts and operating supplies for maintenance of existing essential equipment and activities in laboratories.
6. For any use which the Director of Industry Operations determines necessary and appropriate in the public interest."

● It was announced some time ago that the price ceilings had been removed on synthetic rubber, aviation gasoline, toluene, and materials essential to their manufacture. The significance of this is the implication that these materials are now regarded as among the most important products of chemical industry.

● J. H. Mote, A. R. Conklin, and W. O. Sommerhalter, of the University of Georgia, some time ago sent us a description of a semimicro Victor Meyer method of molecular weight determination. The accompanying figure shows their modified form of apparatus, the advantage of which is that all of the essential parts are in one piece. The calibrated eudiometer tube, *G* (made of 6-mm. tubing), in which the volume of liberated vapor is measured with a mercury-leveling tube, is connected with the main part of the apparatus by a three-way stopcock, *C*. Liquid samples (of from 10 to 30 mg.) are picked up in fine, weighed capillary tubes which are then sealed at one end and weighed again. The capillary is introduced through the ground-glass stopper of *B* (made from the neck of a broken volumetric flask) and supported on the "magnetic valve," *D*, before dropping into the chamber, *A*, surrounded by the steam bath, *H*. The construction of the magnetic valve is shown separately. A piece of glass tubing just large enough to slip easily into the side arm is filled with iron wire or rod and



SEMIMICRO VICTOR MEYER APPARATUS

sealed off. The depression at *E* allows the inner tube to shut off the vertical one satisfactorily, while *F* prevents it from sliding too far down the side arm and breaking *E* on being drawn back with a magnet. The authors report that five or six determinations can be made within an hour, with an average error of about 4 per cent.

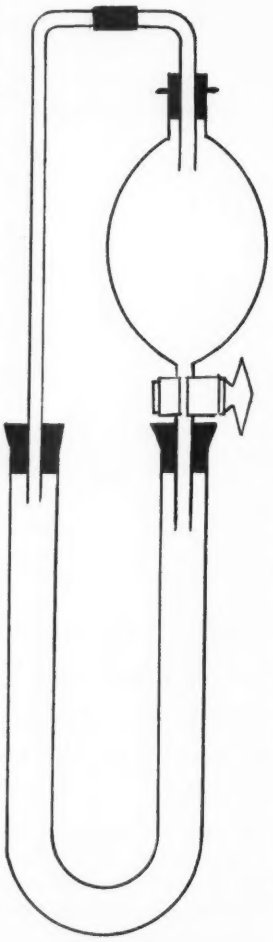
● Uses of Cellophane have been further restricted by orders issued by the Director of Industry Operations. Particular restrictions are for use as window cartons, for carton overwraps, for packaging animal food, rubber nipples, and candy.

"Cellophane and other similar transparent cellulose sheets covered by the order are being used to an increasing extent for essential food packaging, where it replaces tin. The peculiar properties of cellophane—light weight; imperviousness to oil, grease, moisture; flexibility; and durability—make it highly useful for both civilian and military packaging. Cellophane also has a wide variety of military uses for which there is no adequate substitute.

"Conservation of cellophane under this order is to avert a shortage of military and essential supplies, as well as to conserve some of the 50,000 tons of high alpha sulphite wood pulp, thousands of tons of sulphuric acid, large amounts of plasticizers, chlorine, and caustic soda. All these products are critical, and must be conserved for war production wherever possible."

● Claim and reclaim! The Westinghouse Electric and Manufacturing Company claims to have reclaimed enough aluminum from machine shop scraps to build ten Army bombers. After pure aluminum and copper are removed from the scrap the remaining metal is melted into 100-pound ingots. These are tested chemically and sorted into 50 kinds of alloys for reuse.

● We have seen two or three different forms of apparatus to demonstrate the Law of Conservation of Mass, but a new one was brought to our attention recently by Dr. Hermann Bernhard, of St. John's College. A large U-tube and a dropping funnel of suitable size are arranged as shown in the illustration. Two electrolyte solutions are used, one in each, such that a solid precipitate will be formed upon mixing by opening the stopcock. The whole apparatus is suspended upon a demonstration balance while the reaction is carried out, showing that no essential change in total mass occurs. It is also suggested that the demonstration is more effective if the metallic constituent of the precipitate is identified as the same as that in one of the original solutions. An example of this would be the precipitation of silver carbonate by reaction between silver nitrate and sodium carbonate, followed by washing and drying the precipitate and heating strongly until metallic silver results.



● Reinhardt Schuhmann, of the Western State College of Colorado, has outlined a general college course along lines which, although not unique in principle, are nevertheless somewhat radical. He points out that most textbooks of general chemistry are based upon the discussion of *substances*, their properties and behavior, while general chemical principles emerge from this discussion more or less incidentally. He proposes to reverse this relation: to make the general principles primary and fundamental, and discuss the particular properties of elements and their compounds as illustrations. This is scarcely a new idea, of course, but the outline of his particular course, which is too lengthy to reproduce here, emphasizes the theory of atomic structure as an introduction to chemical reactions and an interpretation of chemical behavior. Two types of reactions form the underlying basis for the course—the ionic reaction in water solution as interpreted through the mass action law, and the oxidation-reduction reaction as interpreted through electron exchange.

● A "catechism" issued by the War Manpower Commission contains—among others—the following questions. Comment is superfluous.

Question—I am a die-maker but I want to join the Navy to get a crack at the Japanese—am I right?
Answer—You are wrong. You are more valuable making dies in a war plant.
Question—I operate a sugar-beet farm but I am anxious to abandon it for a job in the arsenal—what do you advise?
Answer—Don't do it—your country needs sugar as much as it needs the explosives made from sugar.
Question—I am a college student majoring in chemistry—should I quit school and look for a job?
Answer—No. Finish your course—you'll be more valuable and more needed as a technician.

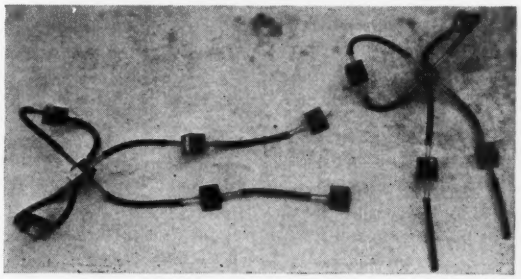
The lesson that has been learned, from the last war as well as the present, is that in modern war everyone must fight, and the question *where* he or she is to fight is something to be decided solely on the basis of need and skill. We cannot afford under any circumstance to rob the armed services of suitable manpower material, nor, on the other hand, can we afford to permit a highly skilled craftsman to be inducted into the armed services unless the armed services have greater need of him than has war industry.

G. M. Evans, of the British Ministry of Labor and National Services, has been quoted as saying:

"It is no good having a large Army if there are not sufficient weapons and equipment with which to fight; it is no good producing vast quantities of munitions of war if there are not trained forces to use them; similarly within the field of supply itself a proper balance must be kept between the needs of munitions industries and those of other industries and services, including the distributive trades, transport services, even finance."

● D. G. Nicholson, of the University of Illinois, presented a paper before the division of Chemical Education at the Memphis meeting in which he summed up the results of a test given to college seniors who were expecting to teach chemistry in high schools, as well as to experienced high-school teachers who were taking advanced work at the University. These people were all given the same Coöperative Chemistry Test (Form 1939) which had been taken by college freshmen. Results revealed a relative weakness on problems and equations, as compared to other items of the test. There was little difference in the accomplishment of college seniors and experienced teachers of high-school chemistry. It was suggested that the notorious weakness of college freshmen in regard to problems and equations may very well be the result of the fact that their high school teachers are themselves too poorly grounded in these fundamentals.

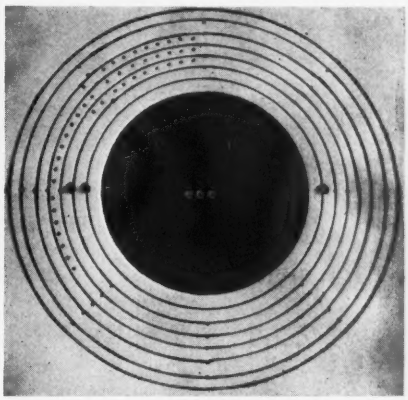
● Two ideas were sent in recently by Nicholas R. Bondoc, of the Fresno, California, High School, and are shown in the accompanying illustrations. The



MOLECULAR MODELS

first is a method of making molecular models out of cubical wooden blocks, wooden pegs, and short lengths of old rubber tubing. The second is an "atomic structure board" on which the structure of different atoms can be shown by inserting pegs of different colors (golf tees are good) to represent electrons or neutrons in the nucleus or various quantum levels.

● We note in the June number of the *American Journal of Physics* a bibliography of "Readings on Interconnections of Science and Society." While we commend it to anyone interested in the current movement of the "socialization of science" we regret to say that not a single reference to the many sources in the JOURNAL OF CHEMICAL EDUCATION has been included. The list is admittedly "selected" but we think the selection might have been more inclusive.



ATOMIC STRUCTURE BOARD

LETTERS

Stick to the Job

To the Editor:

Congratulations on the editorial in the July issue of the JOURNAL OF CHEMICAL EDUCATION.

If you have not yet seen it and studied it, I would urge that you look up General Lewis B. Hershey's Occupational Bulletin No. 10, dated June 18, 1942, on Critical Occupations and Scientific and Specialized Personnel. I believe that this could be made the subject of a very cheering editorial and a return to the attack on this problem of students in chemistry and chemical engineering going into the enlisted reserves. It would seem that, after the issuance of this Occupational Bulletin No. 10, there is no excuse for a student in chemistry or chemical engineering doing anything but stick to his own job and do it the best he can. If he goes into the reserve he is going to be lost to chemistry or chemical engineering, because of the proven fact that the needs of the Army and Navy for chemists and chemical engineers are much smaller than the number of such men they have now.

FRANK C. WHITMORE
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

The Burning of a Candle

To the Editor:

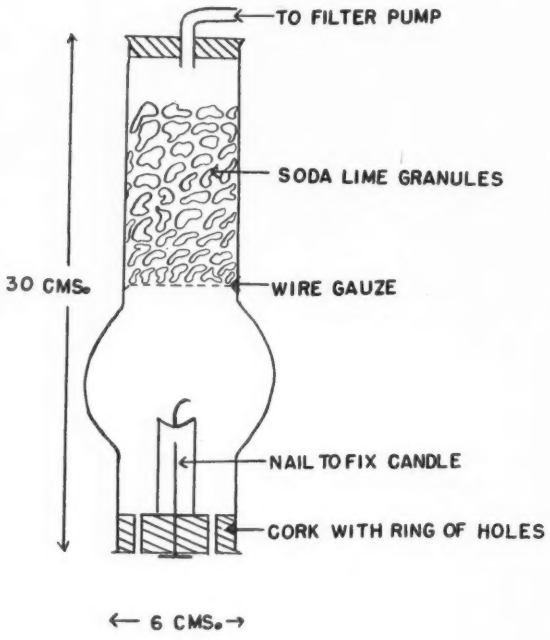
The author of an article in the March, 1941, number states that he has failed to make work the demonstration apparatus described in many textbooks, to demonstrate that the products of combustion of a candle weigh more than the candle. He describes a fairly elaborate apparatus to replace it.

For the past ten years I have kept permanently made up the usual (to me) textbook apparatus. I take it from its shelf once a year, demonstrate it with monotonous success, and put it back for another year. I should say that I have replaced the SODA-LIME (NOT caustic soda) about once in three years.

I append a diagram with dimensions.

The apparatus is counterpoised on an ordinary laboratory balance reading to 0.01 g. The lower cork is removed, the filter pump (working gently) attached to the exit tube, the candle lit and replaced. The experiment is allowed to continue for three minutes. The filter pump is disconnected and the candle then goes out. The gain in weight is 0.3 g., i. e., 0.1 g. per min. and I have found this extraordinarily constant

over a number of years. This is not surprising, for the rate of flow of air is fairly critical. If the pump is not working fast enough the candle goes out; if too fast, the flame is sucked off the wick.



If a control experiment is performed without the candle alight, there is no measurable gain in weight in three minutes; that is, the gain is not due to absorption of atmospheric moisture and carbon dioxide.

JAMES A. WENDEN
CATERHAM SCHOOL
SURREY, ENGLAND

Opportunity Knocking

To the Editor:

I often think it a pity that people set up such formidable objectives for teaching the sciences when they can be so simply expressed in the single word *opportunity*—opportunity to study for a short time a subject that can give our students understanding and appreciation of men and things in relation to themselves and others, and often there comes so great an appreciation of science itself that some of these seek a larger opportunity and decide they want or need more of these essential science facts. They are tomorrow's doctors, nurses, technicians, engineers, and scientists.

GRETA OPPE
BALL HIGH SCHOOL
GALVESTON, TEXAS

For an Heuristic Presentation of Chemistry

To the Editor:

May I offer a word of appreciation for Professor Babor's recent article on "The Sequence of Topics in General Chemistry?" I am gratified to note that Dr. Babor has gone back on the current vogue and has reverted to the older, less "logical" but more teachable order of topics.

I go even a little further. There is a theory, sometimes called "Heuristic," that the developing individual human mind tends to pass through the same stages of concept and comprehension that the human race, as a whole, has followed—just as the human embryo passes through the rudimentary stages of biological evolution. I know of no serious effort to prove this theory: yet it is certain that the average adolescent does not think logically. Any teacher who has investigated the actual ways in which students finally achieve comprehension is likely to be astonished at the curiously involved, inverted, and "back-door" or "intuitive" thought paths of the learner. It seems more than plausible that the average student will grasp the developing theory of any science more naturally and easily if the topics are presented in the historical order of their discovery. Lowry's "Historical Introduction to Chemistry" is an attempt in this direction.

Not many of the fundamental theories of science have been discovered by the method of pure, logical induction. Proust proved the law of definite proportions, and had before him sufficient data to demonstrate the law of multiple proportions—the "logical" foundation of quantitative atomic theory—yet it never occurred to him to apply his figures to atoms. Dalton, groping around in the vast region of his imagination for some workable picture of the mechanical structure of gases, stumbled "intuitively" upon the idea of assigning fixed weights to elementary atoms; perceived that the idea would explain Proust's figures; saw, also, that if his idea was correct, there would have to be a law of multiple proportions, and proceeded to "discover" the law.

The "logical" foundation of present-day chemistry is electronic, atomic-structure theory. Several able teachers have published texts starting from that viewpoint. In some cases, however, in the later editions of their books, they have felt constrained to revert to atoms and molecules as provisional fundamental entities of chemistry and put electronic chemistry one or two hundred pages further on. Any method, of course, can be taught with a degree of success if the teacher is enthusiastic about it, and has teaching ability. But at least some highly intelligent and progressive teachers have abandoned their earlier ambitions and gone back to a less "logical" but apparently more practical order of topics....

GLEN WAKEHAM
UNIVERSITY OF COLORADO
BOULDER, COLORADO

RECENT BOOKS

SCIENCE EDUCATION IN CONSUMER BUYING. *George L. Bush*, Ed. D. Bureau of Publications, Teachers College, Columbia University, New York City, 1941. x + 228 pp. 14 × 22 cm. $2.35.

Several aspects of consumer education digested for use by science teachers are presented. Included is a critical appraisal of sources of consumer education including (1) books, (2) federal government agencies, (3) private testing agencies, and (4) professional associations.

Illustrative consumer-education material covers foods, clothing, shelter, and miscellaneous items. Without adding anything new to either consumer education or science education, this book points out the many areas where the fields overlap, or can be made to coincide.

Arguing that science courses must include substantially greater amounts of consumer education in the future, the theme is carried with enthusiasm to considerable detail. The reader is sometimes left stranded with expressions such as: "Most people purchase a high proportion of their goods health services" (page 4); "Changes in new automobiles are made rather rapidly" (page 12); "Science education faces extraordinary difficulties in connection with the buying of clothing" (page 118); "It is evident that our warm homes, public buildings and automobiles are not at all consistent, from a health standpoint, with the lightweight dresses, thin silk stockings, and flimsy slippers which women wear to brave the snow and subzero temperatures" (page 118); or even the title itself.

ELBERT C. WEAVER

BULKELEY HIGH SCHOOL
HARTFORD, CONNECTICUT

THE DEVELOPMENT OF MINERAL INDUSTRY EDUCATION IN THE UNITED STATES. *Thomas Thornton Read*, E.M., Ph.D., Vinton Professor of Mining Engineering, Columbia University. Foreword by *Herbert Hoover*, Mining Engineer and Ex-President of the United States. First Edition. The American Institute of Mining and Metallurgical Engineers, Inc., New York City, 1941. vii + 298 pp. 26 figs. 15 × 23 cm. $2.00.

According to the preface, the book is the outgrowth of the activities of the Mineral Industry Education Division of the American Institute of Mining and Metallurgical Engineers, organized in 1932. Shortly after organization of the division two facts became evident: "The first was that the men engaged in educational work in this field typically thought of themselves as technologists, and only secondarily (or not at all) as educators. The second was that lack of a common background of general knowledge on the broad subject of education for the mineral industries hampered discussion of educational problems. This was a natural result of the first condition, since no one had taken the time to study the whole field from any viewpoint other than technical content of curricula. The general subject of education has been subjected to much professional study, and it seemed important that the field of special education for the mineral industries should no longer lie fallow."

A brief chapter is devoted to "The Beginnings of Mineral Industry Education" in Europe followed by "American Beginnings," "Mineral Industry Education in the United States," and "Unsuccessful Ventures." The history of the founding of the Columbia School of Mines is traced from the gift of the Geo. T. Strong collection of minerals to Columbia College in 1863. The author apologizes for devoting a chapter to Columbia by saying: "The main reason for according it the dignity of a separate chapter is to emphasize its form of organization, which is believed to have been not only important to itself but also to have influenced subsequent developments elsewhere in a subtle way."

Under the heading "Other Schools," the establishment of mining courses at Harvard, Yale, Michigan, Massachusetts Institute of Technology, Washington and Lee, Lafayette, Rensselaer, Lehigh, Wisconsin, Washington University, Illinois, Vanderbilt, and Case School is briefly discussed. There follows a chapter on "The Rise of State Schools" in which mining schools in California, Colorado, Missouri, Iowa, Ohio, South Dakota, Michigan, Nevada, Alabama, Montana, New Mexico, North Dakota, Utah, Arizona, and Tennessee are briefly reviewed. "Growth in the East" takes up developments in Philadelphia, Boston, and New York. In a chapter entitled "The End of the Century," there is "recorded the initiation of mineral industry education during the period 1890–1910," at a number of institutions.

The final chapters deal with the development of specialized courses such as Petroleum Engineering, Geophysics, Ceramics, Ore Dressing, Metallurgy, and Vocational Education.

The author makes no attempt to give any critical evaluation of the schools discussed, but simply records information about presidencies, faculties, endowments, etc., such as is found in books like "Minerva."

The book is well bound and typographical errors are few. The illustrations of buildings are not especially good, but serve to give some idea of the capital investment in mining education.

FRANK E. E. GERMANN

UNIVERSITY OF COLORADO
BOULDER, COLORADO

LABORATORY MANUAL OF GRAVIMETRIC AND VOLUMETRIC ANALYSIS. *C. R. Johnson*, University of Texas. Texas Book Store, Austin, Texas, 1941. 63 pp. 21 × 27.3 cm. $0.55.

This laboratory manual contains a complete set of representative laboratory exercises for courses in gravimetric and volumetric analysis, with explicit directions for carrying these out; concentrations and quantities of reagents are given precisely. A complete set of analytical report forms is provided; procedures are designed for use in large classes where economy in the use of reagents is important; a simple, rapid, and convenient method of weighing is given. Among the variations in experiments are an improved limestone analysis for use in warmer climates, and a chemical analysis of water by standard procedures.

THE CHEMISTRY OF ORGANIC MEDICINAL PRODUCTS. *Glenn L. Jenkins*, Ph.D., Dean and Professor of Pharmaceutical Chemistry, School of Pharmacy, Purdue University, and *Walter H. Hartung*, Professor of Pharmaceutical Chemistry, School of Pharmacy, University of Maryland. John S. Swift Company, Inc., St. Louis, Missouri, 1941. xii + 457 pp. 16.5 × 24.2 cm. $3.80.

According to the authors, "this volume has been written as a textbook for students who have had basic courses in chemistry and who are interested in the chemistry of medicinal and related products. It is intended primarily for use by students in the more advanced courses in pharmacy. It should prove of value and interest also to practitioners of pharmacy and to students and workers in chemical and medical fields of science." The objective in writing the book has been to organize the large number of organic medicinal compounds according to the accepted scheme of chemical classification. The chemistry of methods of preparation, properties and descriptions of the more important compounds of each class are included. The uses and modes of administration are given so that some idea of the relative importance of the compounds may be gained, although it is expected that details of pharmacology and therapeutics will be studied in texts devoted to those subjects. In many instances where sufficient data are available, correlations between physiological activity and chemical structure are made. A bibliography of general references, divided as to subject, is given.

ORGANIC SYNTHESES. Collective Volume I, being a Revised Edition of Annual Volumes I–IX. *Henry Gilman*, Editor-in-Chief; *Roger Adams, H. T. Clarke, J. B. Conant, C. S. Marvel, C. R. Noller, F. C. Whitmore, C. F. H. Allen*, Formerly Secretary to the Board. Second Edition, Edited by *A. H. Blatt*, Secretary to the Board, Queens College, Flushing, N. Y. John Wiley and Sons, Inc., New York City, 1941. xi + 580 pp. 30 figs. 15 × 23 cm. $6.00.

The second revised edition of ORGANIC SYNTHESES, Collective Volume I, follows exactly the plan of the first edition, which has proved so satisfactory. The few errors present in the first edition have been corrected, and a considerable number of additions and improvements in procedures have been suggested. "New or improved procedures are included for preparing benzamidine hydrochloride, adipic acid, *dl*-alanine, alkyl bromides, benzohydrol, *n*-butyl chloride, β-chloropropionic acid, cyclohexene, diphenic acid, benzoylformic acid, 1,4-naphthoquinone, perbenzoic acid, and platinum catalyst for reductions from platinum scrap or spent catalyst."

Many of the products described in the original Collective Volume I are now available commercially at prices of five dollars or less per kilogram. In such cases the directions for the preparation have been marked with an asterisk, although complete directions are still retained.

The literature citations have been reviewed through *Chemical Abstracts*, Volume **34** for 1940, and many additions are apparent. The references are purposely not complete but logically and carefully selected. There has been added as a subtitle to each preparation the *Chemical Abstracts* indexing name for the compound prepared, when that name differs from the commonly used name.

The editors and publishers have spared no efforts in producing again a useful and attractive volume. Every desirable and essential feature, including the five previous indexes, of the first collective volume has been retained. Every organic chemist and chemical library should have these methods of preparation instantly available. The only consideration will be a decision between the individual volumes and the collective volume. Many will prefer the latter because of its compactness and unified arrangement.

RALPH E. DUNBAR

NORTH DAKOTA STATE COLLEGE
FARGO, NORTH DAKOTA

ENRICHED TEACHING OF SCIENCE IN THE HIGH SCHOOL. *Maxie Nave Woodring*, Associate Professor of Education, Teachers College, Columbia University; *Mervin E. Oakes*, Instructor in Biology, Queens College of the City of New York; and *H. Emmett Brown*, Teacher of Science, Lincoln School, Teachers College, Columbia University. Second Edition. Bureau of Publications, Teachers College, Columbia University, New York City, 1941. xii + 402 pp. 15 × 23 cm. $3.25.

A thoroughly revised and much enlarged source book of materials and publications relating to science and science teaching.

ELBERT C. WEAVER

BULKELEY HIGH SCHOOL
HARTFORD, CONNECTICUT

WE NEED VITAMINS. WHAT ARE THEY? WHAT DO THEY DO? *Walter H. Eddy*, Ph.D., Professor Emeritus in Physiological Chemistry, Teachers College, Columbia University, and *Gessner G. Hawley*, Technical Editor, Reinhold Publishing Corporation. Reinhold Publishing Corporation, New York City, 1941. 102 pp. 12.5 × 18.7 cm. $1.50.

An authoritative, yet easy-to-read book on the vitamins, written simply, and designed primarily for the general reader. The latest values of the vitamin content of foodstuffs are given in handy tabular form—a summary which should prove practical for determining daily needs of the proper vitamin foods. There is very little chemistry, in the way of formulas or structures, in the book, because of its elementary treatment of the subject.

TECHNICAL REPORT WRITING. *Fred H. Rhodes*, Professor of Chemical Engineering, Cornell University. First Edition. McGraw-Hill Book Company, Inc., New York City, 1941. x + 125 pp. 7 figs. 15 × 23 cm. $1.50.

The author has produced a book, written in concise, clear style, which should prove invaluable for helping the technical man to present an adequate report of his work. The topics dealt with are: the importance of effective presentation in technical reports, the characteristics of a good report, the organization of a technical report, the laboratory notebook (preparation good enough so that it may serve as evidence in a patent litigation), the form of a report, hints as to style, conventions, and correct usage, the oral presentation of technical reports, the mathematical analysis of experimental errors, the graphical presentation of data, statistical methods, and the method of dimensional analysis. The appendixes give symbols commonly used in engineering reports; conventions; and references. There is a general subject index.

The material is handled in a most practical manner; the discussions of the simpler mathematical and graphical methods by which the experimental data may be correlated, analyzed, and presented, are valuable additions to the work. Noteworthy features include the application of the method of least squares, a critical analysis of effects of experimental errors, the derivation of correlation coefficients, the estimation of the proper size of sample that must be taken to represent the lot with reasonable accuracy, the special applications of logarithmic, semilogarithmic, and probability cross-section paper, and the construction of nomographs.

FATIGUE OF WORKERS. ITS RELATION TO INDUSTRIAL PRODUCTION. *Committee on Work in Industry of the National Research Council.* Reinhold Publishing Corporation, New York City, 1941. 165 pp. 15 × 23 cm. $2.50.

Prepared by the Committee on Work in Industry of the National Research Council, this volume contains the findings of this group with relation to fatigue of workers, and as such should be of value to every business man, executive, personnel director, or student of industrial relations. The story tells of the methods of investigation used to lead to conclusions concerning physiological and psychological conditions affecting the efficiency of workers. Since the body can adjust itself to ordinary changes in industrial conditions, no single factor in work can be identified as fatigue. A study of the relationship between social and technical organization of the plant, and their slow and rapid reaction to change, respectively, gives suggestions for more harmonious conditions of work.

GLASS: THE MIRACLE MAKER. ITS HISTORY, TECHNOLOGY, AND APPLICATIONS. *C. J. Phillips*, Corning Glass Works. Pitman Publishing Corporation, New York City, 1941. xii + 424 pp. 207 figs. 15 × 23 cm. $4.50.

According to the author, this book is intended "primarily, but not exclusively, for the architect, the civil, mechanical, electrical or chemical engineer, the industrial designer, or other industrial executive—in short, for those who may see in glass a unique and versatile material, interesting in its own right, and full of unexplored possibilities for creating products and improving production methods." Yet the language used is simple and understandable, and the book may be read with profit by those who have only a general interest in the subject, and do not wish to apply the information to particular problems of their own. The volume covers the history and technology of glass making, from earliest days to the present, giving the chemistry, mechanical and physical properties of glass, handling of materials, and details of glass working up to the final inspection of the finished product. Part II, which deals with applications of glass, tells of its uses in architecture and building construction, in the home, in electrical transmission and communication, in illumination, in manufacture, in science and research, and in fiber glass. The book is thoroughly and strikingly illustrated throughout.

INTRODUCTORY ORGANIC CHEMISTRY WITH CERTAIN CHAPTERS OF BIOCHEMISTRY. *E. Wertheim*, Professor of Organic Chemistry, University of Arkansas. The Blakiston Company, Philadelphia, 1942. vii + 482 pp. 82 figs. 15 × 23 cm. $3.00.

This textbook was written primarily for the use of students of home economics, nutrition, agriculture, veterinary science, and pharmacy, as well as for premedical and predental students. The author's aim is to acquaint the student with the fundamentals of structural organic chemistry, the relationships which exist among organic compounds, the practical uses of organic compounds, and to provide an introduction to the study of biochemistry.

In the opinion of the reviewer, the author has succeeded admirably in accomplishing his objective. The introduction is excellent. The free use of graphic formulas and photographs of molecular models in the first part of the book will prove helpful to students. There are excellent charts at the ends of some of the chapters, showing the relationships of the compounds studied. The statements concerning the practical uses of the compounds studied are exceptionally good. The numerous cross references are accurate, except that the reference on page 275, to page 275, should be to page 260. Footnotes containing brief statements about some of the men who discovered certain organic reactions add interest to the book.

The book is well written and is remarkably free of errors. The reviewer does not approve the avoidance of such terms as "optical enantiomorphs," "optical antipodes," and "diastereoisomers," nor the failure to use the clearer cyclic formulas for the disaccharides. It is unfortunate that the brief statement concerning nylon should be in a paragraph describing polymeric anhydrides. The use of chloroacetic acid instead of potassium chloroacetate in the reaction with potassium cyanide is a common error in textbooks.

The discussion of enzymes, hormones, vitamins, digestion and absorption of foods, metabolism, nutrition, foods, and dietary necessities serves as an excellent introduction to these important subjects. The illustrations of vitamin deficiencies in rats are well chosen.

The book has an appendix of thirty-eight pages, containing, among other things, a glossary of chemical, biological, and medical terms, a rather extended discussion of methods for the removal of stains, and a table listing the composition and value of various foods. The glossary could be improved by having only one list instead of subdividing it into (*a*) organic, biological, and medical terms, and (*b*) inorganic terms.

The reviewer does not hesitate to recommend this book without reservations.

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LABORATORY MANUAL FOR INTRODUCTORY COLLEGE CHEMISTRY. *Joseph A. Babor*, Associate Professor of Chemistry, and *Alexander Lehrman*, Associate Professor of Chemistry, College of the City of New York. Thomas Y. Crowell Company, New York City, 1941. iv + 276 pp. Appendix, 30 pp. 56 figs. 22.5 × 28.4 cm. $1.75.

This manual contains more experiments than will probably be used in any one course, thus providing a wide choice. Many simple experiments have been included in the early part to allow the student to become acquainted with simple laboratory technic before going on to more advanced work. The quantitative aspects of chemistry are emphasized throughout, and the limitations of measurements are stressed by calling attention to errors, their sources, magnitude, and their effect on results. Thought questions requiring a careful study of procedure, results, and text references are included at the end of each experiment. A detailed description of the operation of weighing has been omitted, as types of balances and methods differ so widely. A key to references in several recent elementary chemistry texts has been included at the back of the book, so that its use is not restricted to the text by the same authors.

MODERN BREAD FROM THE VIEWPOINT OF NUTRITION. *Henry C. Sherman* and *Constance S. Pearson*, Columbia University. First Edition. The Macmillan Company, New York City, 1942. viii + 118 pp. 13 × 20 cm. $1.75.

This book is planned to meet the need of dietitians engaged in teaching the public and the nutritionally minded consumer. Valuable information is collated on the nutritive value of bread and the background of the present bread enrichment program. It is the best book of its kind yet published. The chapter on the fundamental characteristics of bread as a food is excellent. The important part bread plays in the diet of western civilization is clearly brought out. The chapters on proteins, minerals, and vitamins of bread are interestingly written and cover the essential facts. The authors mention the almost universal use of dough conditioners which regularly contain calcium salts. The use of these conditioners has raised the calcium content of bread over a long period of years, and it is paradoxical that it requires emergency conditions for the realization of the nutritional importance of such a valuable and almost universal commercial practice. It is gratifying that such an authority as Dr. Sherman now favors the use of dough conditioners because of their lime content. An analogous situation existed in England. The Minister of Foods questioned the use of lime salts in baking, but now the Minister of Health demands the addition of lime salts to all white flour and bread. It is regrettable, however, that more complete tables are not given for the amounts of minerals and vitamins in serving portions of bread. Such information would be informative for the readers to whom the book is directed. The chapters on the enrichment program from the legal and technological viewpoints are well handled.

Too much emphasis is given to the nutritional value of whole wheat bread in view of the fact that the public overwhelmingly demands white breads. All types of breads such as whole wheat, rye, graham, wheat germ breads, have been, and are available, but yet 98 per cent of the public demand white bread. The authors are somewhat unjust to the cereal chemists, whom, the authors claim, strive only for improvement of baking quality and bread texture. Good bread texture is absolutely necessary under modern merchandising conditions in that a loaf of good texture maintains its taste appeal longer than a coarse textured loaf. Unfortunately the authors suggest that wheat germ may be used to enrich white bread up to the whole wheat level for vitamins and minerals. In the first place the quantity of wheat germ required would render the loaf unappetizing, and secondly there would not be enough wheat germ to go around. The authors stress the value of milk in bread and rightly so, but they fail to mention the fact that by-products of white flour milling such as middlings, germ, and bran are perhaps our largest and best source of cattle food—making it possible to have an abundance of relatively cheap milk. From one viewpoint it is perhaps advantageous to have the cows convert such by-products to milk rather than attempt to utilize them directly in human nutrition. Considerable mention is given to the value of "peeled" whole wheat flour, but it is doubtful if any appreciable improvement has resulted over the processes now in use for cleaning and scouring wheat before it is ground into flour. The authors show by animal feeding that the diet may safely include 40 per cent enriched white bread; yet the suggestion is made many times that whole wheat bread be used instead of white breads—this suggestion being almost impossible of accomplishment because of public preference for white bread. The use of 40 per cent enriched white breads in our diets, especially of the low income groups, would be advantageous both from the nutritional and economical points of view.

The book is interestingly written. The material illustrating the method of approach of modern biochemical research is informative. Dietitians, consumers, and students in home economics courses will find the book of value.

CHARLES HOFFMAN
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GASTON DALBY

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NEW YORK CITY

SEMIMICRO QUALITATIVE ANALYSIS. (THE BARBER PRESSURE BULB METHOD.) *Hervey H. Barber*, Ph.D., Associate Professor, and *T. Ivan Taylor*, Ph.D., Assistant Professor, School of Chemistry, University of Minnesota. Harper and Brothers, New York City and London, 1942. xvi + 446 pp. 2 plates, 54 figs. 15.4 × 23.5 cm. $3.50.

This text for students beginning qualitative analysis is divided into Part One, Theory, pages 1 to 194; Part Two, Experimental Direction, pages 195 to 378; and Part Three, Reference Tables, etc., pages 379 to 422.

The theoretical part of this text is well organized, well written, and adequate. Both the Debye-Hückel and Brønsted-Lowry theories are used. Teachers who like a complete exposition of the physical chemistry of the nature of electrolytes and their behavior in water solutions will like the theory part of this book. On the other hand teachers with limited time for the course may be unable to cover all of the theoretical material presented. A minor fault is the use, in spots, of the words "base" and "basic" in both the Arrhenius and Brønsted senses.

In the experimental part of the text the authors have made a new and distinctive contribution to the mechanics of semimicro qualitative analysis without the use of centrifuges. To separate precipitates from filtrates the "Barber Pressure Bulb Method" [*Ind. Eng. Chem., Anal. Ed.*, **12**, 58 (1940)] is employed. In this method a pear-shaped rubber medical syringe is used to produce either suction or pressure filtration. The reviewer has tried these filtering expedients and testifies that they are entirely practical. Whether the filtration methods just described are superior to centrifuges or other small scale filtering devices is a question involving many factors and is one which the reviewer leaves to the attrition of time and experience to answer. The number of solutions and reagents required is noteworthy. Pages 210, 211, and 213 list a total of 95 items which includes 41 inorganic reagents, 25 organic reagents, 5 indicators, and 24 test solutions. Figures 50, 51, and 52, presumably pictures of the required solution bottles and racks, contain the pictures of 119 bottles.

The typography and binding of the book are excellent.

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EXPERIMENTAL PHYSICAL CHEMISTRY. *W. G. Palmer*, M.A., Sc.D., D.Sc., Fellow of St. John's College, Cambridge, University Lecturer in Chemistry in the University of Cambridge. First Edition. University Press, Cambridge; The Macmillan Company, New York City, 1941. xii + 321 pp. 89 figs. 13 × 21 cm. $2.75.

This volume presents material for a laboratory course in the conventional fields of physical chemistry with the addition of chapters on the properties of crystals and on surface chemistry in which more recent developments are emphasized. Each chapter includes (*a*) a brief set of notes introducing the subject under consideration, (*b*) detailed directions for conducting the experiments, and (*c*) completely worked examples of nearly all the experiments. The author states in the preface that the introductory notes are not intended, "to replace the use of adequate text books on the theory of the subject," but rather to offer to the students ready access to principles while at work on an experimental problem. Regarding the detailed instructions the author takes the following position, "I venture to counter the criticism that the practical instructions are so detailed as to impugn the students' initiative, by remarking that if a beginner spends the greater part of his limited laboratory period in merely prospecting an experiment, with no satisfying result, discouragement will commonly overshadow all that he may well have learnt in manipulation." A noteworthy feature of the book is "the choice and nature of the experiments, necessitating the simplicity of home-made apparatus and sometimes the substitution of rough and ready means of observation for less direct methods, which would overtax both the time and experience of the beginner."

In the opinion of the reviewer, the above objectives have been reached most successfully. The theoretical discussions, while of necessity brief, appear to be consistently sound and pertinent. The laboratory directions are carefully stated in detail and one receives the impression that the student who uses them should not go far wrong. In general, a number of experiments are presented in each field, thus making it possible to make a selection or to use the manual for courses in which varying amounts of time are available for laboratory work. The reviewer was frequently impressed by the ingenuity of the "rough and ready" methods mentioned by the author. This book is remarkably free from misstatements of fact or typographical errors. The job of printing and binding is excellent.

The reviewer does not hesitate to recommend this book to teachers who prefer a laboratory course in physical chemistry with simplified technic. It should be especially useful in wartime when more complex apparatus may well become prohibitively expensive if indeed obtainable at all.

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THIS CHEMICAL AGE. *Williams Haynes*. First Edition. Alfred A. Knopf, New York City, 1942. x + 385 + xxii pp. 18 figs. 2 charts. 15 × 23 cm. $3.50.

THIS CHEMICAL AGE comes nearer to being a textbook for a laymen's course in modern industrial chemicals than any so far published. With the presentation of a few formulas by the instructor, it might well be used for that purpose. The book is written in popular vein to keep the public from being scared away, but the chemistry is presented also, for those who will look for it. The author is trying to perform a service to chemistry such as Paul de Kruif has done for the biological sciences, and he has succeeded in large measure.

The contents are hidden in chapter headings such as "In Vitro: In Vivo," "The Elastic Eldorado," and "The Skeleton in the Vegetable Closet." Behind these titles are the fascinating stories of research men and the industrial development of the new fabrics, synthetic rubber, plastics, resins, "sulfa" drugs, dyes, synthetic camphor, and perfumes.

This book deserves a place on high-school and college science library shelves as well as on popular non-fiction lists.

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HANDBOOK OF CHEMISTRY AND PHYSICS. A READY-REFERENCE BOOK OF CHEMICAL AND PHYSICAL DATA. *Charles D. Hodgman*, M.S., Associate Professor of Physics, Case School of Applied Science, Editor-in-Chief; and *Harry N. Holmes*, Ph.D., Professor of Chemistry, Oberlin College, Associate Editor. Twenty-Fifth Edition. Chemical Rubber Publishing Company, Cleveland, 1941. xviii + 2503 pp. 11.9 × 18.2 cm. $3.50.

This is the usual standard handbook of reference material, with new and revised material bringing it up to date. A table of natural secants and cosecants has been added to the mathematical section; tables covering an ample range of values for the direct conversion of pressure in inches or centimeters of mercury to millibars have been included; abbreviations and symbols have been completely revised in accordance with the recommendations of the Committee of the American Association of Physics Teachers; material on the amino acids, isotopes, photographic plate and film speeds, and vitamins has been revised.

PORTRAITS OF FAMOUS PHYSICISTS. With Biographical Accounts. *Henry Crew*. Scripta Mathematica, New York City, 1942. 64 pp. 26 figs. 25.6 × 35.1 cm. $3.75.

Portraits, suitable for framing, of the following famous physicists: Galileo, Huygens, Newton, Ampère, Fresnel, Faraday, Joule, Clausius, Maxwell, Gibbs, Hertz, and Rowland. The brief biographical sketches are good and to the point, emphasizing the work of each man. Pen and ink sketches and facsimiles of documents also illustrate the text.